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TITLE: ACRYLATE RESIN FOR OPTICAL MATERIAL AND OPTICAL MATERIAL MADE THEREFROM

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INVENTOR-INFORMATION:

NAME

KAWASATO, HIRONOBU

FUJISHIRO, KOICHI

TERAMOTO, TAKEO

SHIRAISHI, KAZUTO

ASSIGNEE-INFORMATION:

NAME

NIPPON STEEL CHEM CO LTD

NIPPON STEEL CORP

COUNTRY

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ABSTRACT:

PROBLEM TO BE SOLVED: To obtain an acrylate resin which yellows little when subjected to a weather resistance test and a heat resistance test and therefore has an increased degree of freedom of the amount of additives such as a stabilizer by specifying the hue of a fluorenehydroxypropyl acrylate.

SOLUTION: This resin comprises an acrylate resin represented by formula I (wherein R is hydrogen or methyl; and (n) is an integer of 0-20) and having a hue (APHA) of 300 or below. The acrylate resin is obtained by reacting diglycidyl ether represented by formula II (wherein (n) is an integer of 0-20)

and having a hue (APHA) of 200 or below with (meth)acrylic acid.

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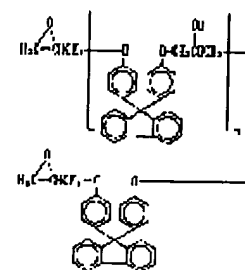
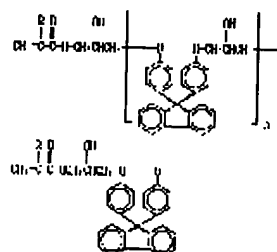
(72)Inventor : KAWASATO HIRONOBU  
FUJISHIRO KOICHI  
TERAMOTO TAKEO  
SHIRAISHI KAZUTO

(54) ACRYLATE RESIN FOR OPTICAL MATERIAL AND OPTICAL MATERIAL MADE THEREFROM

(57)Abstract:

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(71)出願人 000006644

新日鐵化学株式会社

東京都中央区新川二丁目31番1号

(71)出願人 000006655

新日本製鐵株式会社

東京都千代田区大手町2丁目6番3号

(72)発明者 川里 浩信

神奈川県川崎市中原区井田1618番地、新日本製鐵株式会社技術開発本部内

(72)発明者 藤城 光一

神奈川県川崎市中原区井田1618番地、新日本製鐵株式会社技術開発本部内

(74)代理人 弁理士 成瀬 勝夫 (外1名)

最終頁に続く

(54)【発明の名称】 光学材料用アクリレート樹脂及びこれを用いた光学材料

(57)【要約】

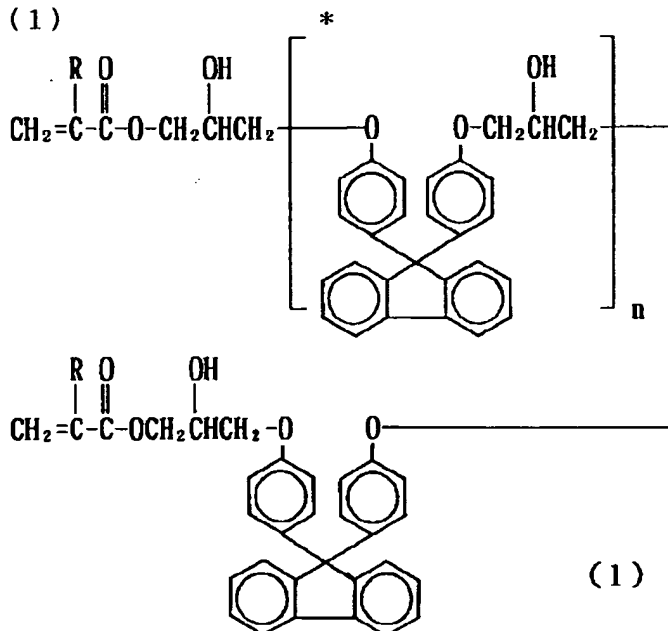
【課題】 耐候性試験時や耐熱性試験時における黄変が少なく、これによって安定剤等の添加剤を添加する量的自由度が増し、また、同じ添加量であれば硬化膜の黄変の程度を低減でき、しかも、クラックの発生も可及的に防止できる光学材料用アクリレート樹脂組成物を提供する。また、かかる光学材料用アクリレート樹脂組成物を用いた透明プラスチック保護用コーティング材料、カラーフィルター用材料及び光学用接着剤を提供する。

【解決手段】 色相APHA300以下のフルオレンヒドロキシプロピルアクリレート樹脂からなる光学材料用アクリレート樹脂組成物である。また、このような光学材料用アクリレート樹脂組成物と重合開始剤とを必須成分として含む透明プラスチック保護用コーティング材料、カラーフィルター用材料又は光学用接着剤である。

## 【特許請求の範囲】

【請求項1】 下記一般式(1)

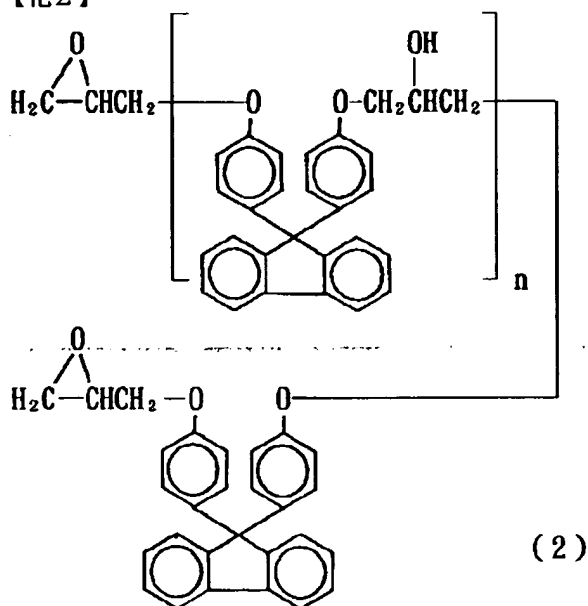
## \*【化1】



(但し、式中Rは水素原子又はメチル基の何れかを示し、nは0～20の整数である)で表される色相APHA300以下のアクリレート樹脂からなることを特徴とする光学材料用アクリレート樹脂。

【請求項2】 アクリレート樹脂が、色相APHA200以下の下記一般式(2)

## 【化2】



(但し、式中nは0～20の整数である)で表されるジグリシジルエーテルと(メタ)アクリル酸とを反応させて得られたものである請求項1に記載の光学材料用アクリレート樹脂。

【請求項3】 必須成分として請求項1又は2に記載の光学材料用アクリレート樹脂と重合開始剤とを含むこと

20※料。

【請求項4】 必須成分として請求項1又は2に記載の光学材料用アクリレート樹脂と重合開始剤とを含み、かつ、必要に応じて顔料を含むことを特徴とするカラーフィルター用材料。

【請求項5】 必須成分として請求項1又は2に記載の光学材料用アクリレート樹脂と重合開始剤とを含むことを特徴とする光学材料用接着剤。

## 【発明の詳細な説明】

## 【0001】

30 【発明の属する技術分野】この発明は、塗膜を形成した際に透明性に優れているだけでなく、硬さ、耐候性、耐熱性及び密着性等においても優れた性能を有する光学材料用アクリレート樹脂及びこれを用いた光学材料に関する。

## 【0002】

40 【従来の技術】従来より、レンズ、LED、プラスチックフィルム、基板、光ディスク等の透明プラスチック光学材料の表面を保護する保護用コーティング材料や光学接着剤、更には液晶表示装置、撮像素子等のカラーフィルター等の光学材料や電子材料の硬化膜を形成するものとして、フルオレンヒドロキシプロピルアクリレート樹脂を主成分とするアクリレート樹脂を用いることが提案されている(特開平3-106918号、特開平3-205417号、特開平5-194338号、特開平4-351674号、特開平4-345608号、特開平4-337307号)。

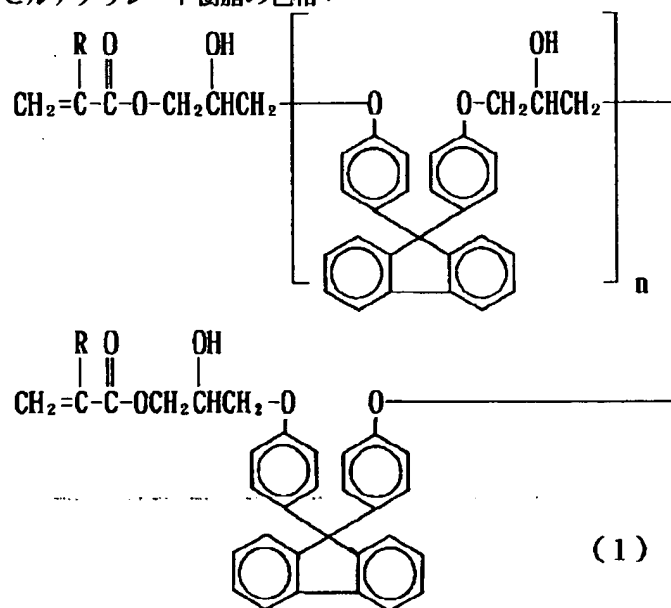
【0003】このアクリレート樹脂は、これを硬化させて得られる硬化膜が耐熱性や耐湿性に優れているだけでなく、低硬化収縮率、鉛筆硬度、耐薬品性、耐電解腐食

着性等において優れた性能を有し、光学材料や電子材料等において広範に用いられる保護膜等の用途への適用が期待されている。

【0004】しかしながら、このアクリレート樹脂をレンズ、LED、光ディスク等の光学材料の表面を保護する保護用コーティング材料や光学接着剤として、あるいは、カラーフィルター等の用途に用いる場合に、耐候性や耐熱性の向上を目的として紫外線吸収剤、光安定剤、酸化防止剤、熱重合防止剤等の添加剤を添加すると、耐候性試験時や耐熱性試験時において形成された硬化膜が黄変し、これら保護用コーティング材料や光学材料用接着剤、あるいは、カラーフィルター用材料として使用できない場合がある。また、この問題の発生を未然に防止するためにこれらの添加剤の添加量を少なくすると耐候性や耐熱性等が必ずしも充分でないという問題が残る。

【0005】

【発明が解決しようとする課題】そこで、本発明者らは、安定剤等の添加剤を添加した際に生じる硬化膜の黄変という問題を可及的に防止し、これによってアクリレート樹脂が有する特性を最大限に生かすことのできる光学材料用アクリレート樹脂について鋭意検討した結果、フルオレンヒドロキシプロピルアクリレート樹脂の色相\*



(但し、式中Rは水素原子又はメチル基の何れかを示し、nは0～20の整数である)で表される色相APHA300以下のアクリレート樹脂からなる光学材料用アクリレート樹脂である。

【0009】また、本発明は、このような光学材料用アクリレート樹脂を用いた透明プラスチック保護用コーティング材料、カラーフィルター用材料、又は、光学材料用接着剤である。

【0010】本発明において、一般式(1)で表される色相APHA300以下のアクリレート樹脂(以下、単

\*をAPHA300以下に抑制することにより、耐候性試験時や耐熱性試験時における黄変が少なく、これによって安定剤等の添加剤を添加する量的自由度が増し、また、同じ添加量であれば硬化膜の黄変の程度を低減でき、しかも、クラックの発生も可及的に防止できる光学材料用アクリレート樹脂が得られることを見出し、本発明を完成した。

【0006】従って、本発明の目的は、耐候性試験時や耐熱性試験時における黄変が少なく、これによって安定剤等の添加剤を添加する量的自由度が増し、また、同じ添加量であれば硬化膜の黄変の程度を低減でき、しかも、クラックの発生も可及的に防止できる光学材料用アクリレート樹脂を提供することにある。

【0007】また、本発明の他の目的は、かかる光学材料用アクリレート樹脂を用いた透明プラスチック保護用コーティング材料、カラーフィルター用材料及び光学材料用接着剤を提供することにある。

【0008】

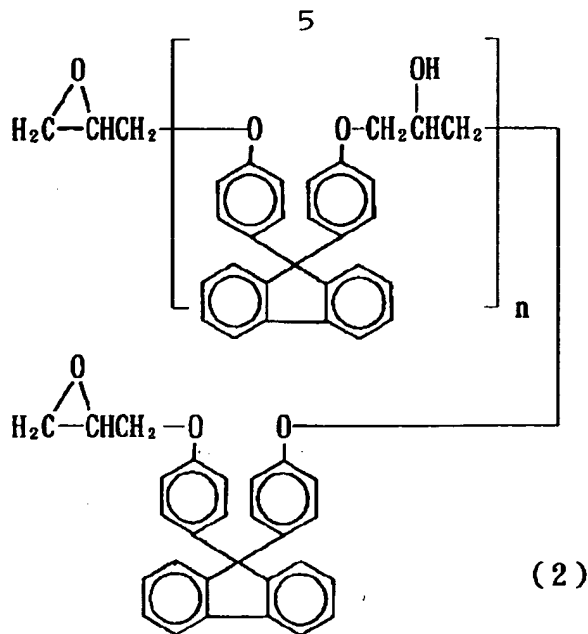
【課題を解決するための手段】すなわち、本発明は、下記一般式(1)

【化3】

40※製造される。まず、9,9-ビス(4-ヒドロキシフェニル)フルオレンとエピクロヒドリンとを塩基触媒の存在下に反応させ、下記式(2)

【0011】

【化4】



(但し、式中 $n$ は0～20の整数である)で表されるジグリシジルエーテル(以下、単に「エポキシ化合物」と称する)を合成する。この反応の際に、9,9-ビス(4-ヒドロキシフェニル)フルオレンとエピクロヒドリンの反応モル比を変えることによって繰り返し数 $n$ を制御することができ、この繰り返し数 $n$ の値はGPC測定で求めることができる。

【0012】次に、このようにして得られた式(2)のエポキシ化合物と下記一般式(3)

【化5】



(但し、式中 $R$ は水素原子又はメチル基の何れかを示す)で表される(メタ)アクリル酸とを反応させ、一般式(1)の原料樹脂を得る。ここで、APHA300以下の色相の原料樹脂を得るためには、式(2)のエポキシ化合物と一般式(3)の(メタ)アクリル酸との反応において、以下のような条件を満足させるのがよい。

【0013】まず、式(2)のエポキシ化合物については、少なくともAPHA300以下の色相のものを使用する必要がある、好ましくはAPHA200以下の色相のものを使用する。この式(2)のエポキシ化合物の色相がAPHA300を超えると、生成される原料樹脂の色相APHAを300以下にすることが困難になる。また、この式(2)のエポキシ化合物の色相がAPHA200以下であると、反応温度や反応時間についての選択の自由度が増す。

【0014】また、式(2)のエポキシ化合物と一般式(3)の(メタ)アクリル酸との反応においては、エポキシ化合物100当量に対して(メタ)アクリル酸を90～110当量、好ましくは90～102当量の割合で

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り少ないと、このものをコーティング剤として用いた時の光硬化時の架橋密度が低下して好ましくなく、また、110当量より多くなると、未反応(メタ)アクリル酸が残存してコーティング膜として耐候性が低下する。

【0015】そして、この反応の際には、必要により、2,6-ジ-*tert*-ブチル-4-ヒドロキシトルエン、ハイドロキノンモノメチルエーテル、*tert*-ブチルカテコール、フェノチアジン等の重合禁止剤や、トリエチルベンジルアンモニウムクロライド、トリエチルアミン、ベンジルジメチルアミン、メチルトリエチルアンモニウムクロライド、トリフェニルホスフィン、テトラエチルアンモニウムブロマイド等の触媒や、必要に応じて粘性調整のために添加されるメチルセロソルブアセテート、エチルセロソルブアセテート、ブチルセロソルブアセテート、ジエチレングリコールモノエチルエーテルアセテート、ジエチレングリコールジメチルエーテルアセテート、プロピレングリコールモノメチルエーテルアセテート、 $\gamma$ -ブチロラクトン等の反応温度以上の沸点を持つ溶剤を添加する。

【0016】ここで、重合禁止剤の使用量は、反応原料混合物に対して1重量%以下、好ましくは0.5重量%未満であり、触媒の使用量は、反応原料混合物に対して0.001～5重量%、好ましくは0.001～3重量%であり、溶剤の使用量は、反応原料混合物に対して5～500重量%、好ましくは5～200重量%である。重合禁止剤の使用量が1重量%を超えると、コーティング剤として用いた時に硬化時の塗膜の架橋密度が上がらず、硬度不足、密着性不良等の問題が起こる。また、触媒の使用量が0.001重量%未満であると、反応系中にゲル化物が発生するという問題が起こる。更に、溶剤を5重量%以上添加することは反応時の粘性低下に有効であるが、500重量%を超えて添加すると反応時間が長くなって好ましくない。

【0017】また、これらエポキシ化合物と(メタ)アクリル酸の反応条件は、反応温度が通常90～130℃、好ましくは95～125℃であって、反応時間が通常3～24時間、好ましくは4～18時間である。反応温度が130℃を超えたり、及び/又は、反応時間が24時間を超えると、色相APHA300以下の原料樹脂を得るためには少なくとも色相APHA200以下の式(2)のエポキシ樹脂を使用する必要性が生じ、反対に、反応温度が90℃未満であると反応時間が極端に長くなりすぎ、また、反応時間が3時間未満であると、反応温度を高くする必要性が生じて好ましくない。更に、二重結合部の重合を抑えるために、通常は反応系内に乾燥空気を吹き込みながら行うのがよい。

【0018】ところで、色相がAPHA300以下、好ましくはAPHA200以下である式(2)のエポキシ化合物を得るには、その製造原料であるビス(ヒドロキ

0以下のものを用いる必要がある。この製造原料のビス(ヒドロキシフェニル)フルオレンの色相がAPHA200を超えると、色相APHA300以下のエポキシ化合物を得るのが困難になる。なお、このような色相APHA200以下のビス(ヒドロキシフェニル)フルオレンを得るには、その製造原料の一種であるフルオレンンについて蒸留精製して酸化触媒のアルカリ、重金属の含有量を1重量%未満としたものを使用したり、あるいは、製造原料のビスフェノールとして精製、再結晶したビスフェノールを用いる必要がある。

【0019】更に、色相APHA300以下、好ましくはAPHA200以下の式(2)のエポキシ化合物を得るには、製造原料のビス(ヒドロキシフェニル)フルオレン中の残存フルオレンを1重量%未満に抑える必要があるほか、グリシジルエーテル化反応の際に反応系内を窒素等の不活性ガスで置換して酸素を除去したり、グリシジルエーテル化反応後に行う残存エピクロヒドリンの除去操作を150℃以下で行ったり、更には、最終段階の脱溶剤化の際の温度を180℃以下で行うのがよい。

【0020】このようにして得られた色相APHA300以下のフルオレンヒドロキシアロピルアクリレート樹脂からなる光学材料用アクリレート樹脂に、少なくとも重合開始剤を配合することにより、以下に説明する透明プラスチック保護用コーティング材料、カラーフィルター材料又は光学材料用接着剤が調製される。

【0021】先ず、透明プラスチック保護用コーティング材料については、上記本発明の光学材料用アクリレート樹脂に必須成分として重合開始剤を配合し、更に必要に応じて、硬度付与や密着性向上のための架橋剤、粘度調整のための反応性希釈剤、レベリング剤等が添加される。

【0022】ここで、このような透明プラスチック保護用コーティング材料を調製する上で用いる重合開始剤としては、光重合開始剤と熱重合開始剤とが挙げられる。光重合開始剤としては、具体的には、ベンゾフェノン、2,2-ジメトキシ-2-フェニルアセトフェノン、2,2-ジエトキシ-2-フェニルアセトフェノン、2-エチルアントラキノン、2,4-ジエチルチオキサントン、ジイソプロピルチオキサントン、ベンジルジメチルケタール、2-ヒドロキシシクロヘキシルフェニルケトン、2-ヒドロキシ-2-メチル-1-フェニルプロパン-1-オン、2-メチル-1-[4-(メチルチオ)フェニル]-2-モルホリノプロパン-1-オン等が挙げられる。

【0023】また、熱重合開始剤としては、公知の過酸化系開始剤やアゾビス系開始剤を使用することができ、過酸化系開始剤としては、具体的には、メチルエチルケトンパーオキシド、メチルイソブチルケトンパ

ルシクロヘキサントンパーオキシド、アセチルアセトンパーオキシド等のケトンパーオキシド系のものや、イソブチルパーオキシド、m-クロロベンゾイルパーオキシド、2,4-ジクロロベンゾイルパーオキシド、 $\alpha$ -メチルベンゾイルパーオキシド、ビス-3,5,5-トリメチルヘキサノイルパーオキシド等のジアシルパーオキシド系のものや、2,4,4-トリメチルペンチル-2-ハイドロパーオキシド、ジイソプロピルベンゼンハイドロパーオキシド、クメンハイドロパーオキシド、*t*-ブチルハイドロパーオキシド等のハイドロパーオキシド系のものや、ジクミルパーオキシド、2,5-ジメチル-2,5-ジ(*t*-ブチルパーオキシ)ヘキサン、1,3-ビス(*t*-ブチルパーオキシイソプロピル)ベンゼン、*t*-ブチルクミルパーオキシド等のジアルキルパーオキシド系のものや、1,1-ジ-*t*-ブチルパーオキシ-3,3,5-トリメチルシクロヘキサン、2,2-ジ-*t*-ブチルパーオキシ)ブタン、4,4-ジ-*t*-ブチルパーオキシ吉草酸-*n*-ブチルエステル等のパーオキシケタール系のものや、2,4,4-トリメチルペンチルパーオキシフェノキシアセテート、 $\alpha$ -クミルパーオキシネオデカノエート、*t*-ブチルパーオキシベンゾエート、ジ-*t*-ブチルパーオキシトリメチルオジベート等のアルキルパーエステル系のものや、ジ-*t*-メチキシブチルパーオキシジカーボネート、ジ-2-エチルヘキシルパーオキシジカーボネート、ビス(4-*t*-ブチルシクロヘキシル)パーオキシジカーボネート、ジイソプロピルパーオキシジカーボネート等のパーカーボネート系のものや、その他のアセチルシクロヘキシルスルフォニルパーオキシジカーボネート、*t*-ブチルパーオキシアリルカーボネート等のものが挙げられ、また、アゾビス系開始剤としては、具体的には、1,1'-アゾビスシクロヘキサン-1-カルボニトリル、2,2'-アゾビス-(2,4-ジメチルバレロニトリル)、2,2'-アゾビス-(4-メトキシ-2,4-ジメチルバレロニトリル)、2,2'-アゾビス-(メチルイソブチレート)、 $\alpha$ , $\alpha'$ -アゾビス-(イソブチロニトリル)、4,4'-アゾビス-(4-シアノバレイン酸)等が挙げられる。

【0024】これらの光重合開始剤や熱重合開始剤は、その何れかを単独で用いることができるほか、2種以上の混合物として使用することもでき、その使用量は、一般式(1)で示される光学材料用アクリレート樹脂並びに後述する重合性の多官能アクリレート化合物、反応性希釈剤の総計100重量部に対して、前者の光重合開始剤は0.1~30重量部、好ましくは20重量部以下であり、後者の熱重合開始剤は0.1~10重量部である。配合範囲がこの範囲を下回ると、重合速度が遅くなって硬化不足となる虞があり、反対に、この範囲を上回



する密着性低下の原因になる。

【0025】また、必要に応じて添加される架橋剤については、トリス（アクロキシエチル）イソシアヌレート（東亜合成社製：M315）、ジペンタエリスリトールトリ（メタ）アクリレート、ジペンタエリスリトールテトラ（メタ）アクリレート、ジペンタエリスリトールペンタ（メタ）アクリレート、ジペンタエリスリトールヘキサ（メタ）アクリレート、トリペンタエリスリトールトリ（メタ）アクリレート、トリペンタエリスリトールテトラ（メタ）アクリレート、トリペンタエリスリトールペンタ（メタ）アクリレート、トリペンタエリスリトールヘキサ（メタ）アクリレート等の3官能性架橋剤が挙げられ、これらは1種のみを単独で用いてもよいほか、2種以上を併用してもよい。この架橋剤の配合割合は、目的とする用途、硬度等の性能によるが、樹脂組成物中の重合性樹脂成分（含量、充填剤、溶剤、重合開始剤を除く）のうち、通常、20～90重量%である。

【0026】更に、必要に応じて添加される反応性希釈剤については、例えば、エチレングリコールジメタクリレート（EGDM）、イソボルニルアクリレート（共栄社化学社製：IB-XA）、N-ビニルピロリドン、テトラヒドロフルフリルアクリレート（共栄社化学社製：THF-A）、カプロラクトン変性テトラヒドロフルフリルアクリレート等が挙げられ、これらは1種のみを単独で用いてもよいほか、2種以上を併用してもよい。この反応性希釈剤の配合割合は、塗布法による適正粘度によるが、重合性樹脂成分のうち80重量%未満で用いられる。

【0027】本発明の透明プラスチック保護用コーティング材料は、例えばレンズ、LED、プラスチックフィルム、基板、光ディスク等の透明プラスチック光学材料の用途に有用であり、例えばスピンコート法により表面に塗布し、低圧又は高圧水銀灯やキセノン灯等を用いて紫外線を照射して硬化させるか、若しくは、ホットプレート、オーブン、赤外線加熱炉等を用いて加熱して硬化させ、光学材料等の表面にコーティング膜を形成せしめる。

【0028】また、カラーフィルター用材料については、上記本発明の光学材料用アクリレート樹脂に必須成分として前記と同様の重合開始剤を配合し、更に必要に応じて、アントラキノン系顔料、ペリレン系顔料、ジスアゾ系顔料、イソインドリン系顔料、ハロゲン化フタロシアニン系顔料、カーボン、チタンカーボン、酸化鉄等の顔料や、フェノールノボラック型エポキシ樹脂、クレゾールノボラック型エポキシ樹脂、トリスフェノールメタン系エポキシ樹脂、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂等の他のエポキシ樹脂や、更にはこれらエポキシ樹脂と（メタ）アクリル酸とを反応させて得られるエポキシ（メタ）アクリレ-

カルボン酸又はその無水物とを反応させて得られる反応生成物等の高分子不飽和基含有樹脂や、2-ヒドロキシエチル（メタ）アクリレート、ベンジルアクリレート、ジペンタエリスリトールヘキサアクリレート、トリメチロールプロパントリ（メタ）アクリレート、ペンタエリスリトールトリ（メタ）アクリレート、ジエチレングリコール（メタ）アクリレート等の重合可能な単官能並びに多官能（メタ）アクリル酸エステル類や、前述した2-メチル-1-[4-(メチルチオ)フェニル]-2-モルホリノプロパン-1-オン等の光重合開始剤や、イソブチルパーオキシド等の過酸化物類や、N、N-ジメチルアミノ安息香酸エチルエステル、N、N-ジメチルアミノ安息香酸イソアミルエステル、トリエタノールアミン、トリエチルアミン等の光増感剤や、その他シランカップリング剤、光安定剤、酸化防止剤等の公知のカラーフィルター用の添加剤が添加される。

【0029】本発明のカラーフィルター用材料は、顔料を添加することなくカラーフィルターの保護膜用の樹脂組成物として用いることができるほか、顔料を添加してカラーフィルターのインキとして用いることもできる。そして、これらカラーフィルター用の保護膜用樹脂組成物やインキは、従来公知の保護膜用樹脂組成物やインキと同様に使用することができ、耐熱性、平坦性に優れた保護膜や微細パターンを形成することができる。

【0030】更に、光学材料用接着剤については、本発明の光学材料用アクリレート樹脂に必須成分として前記と同様の重合開始剤を添加し、更に必要に応じて密着性や靱性を与える反応性希釈剤、ガラス基板との密着性を与えるシランカップリング剤、粘度調整のための溶剤、増感剤等が添加される。

【0031】この光学材料用接着剤中に必要に応じて添加される反応性希釈剤としては、2-ヒドロキシエチルアクリレート（HEA）、2-ヒドロキシエチルメタクリレート（HEMA）、テトラヒドロフルフリル（メタ）アクリレート、イソボルニル（メタ）アクリレート、N-ビニルピロリドン等の密着性付与や粘性調整を目的とするものや、トリエチレングリコールジアクリレート（3E GA）、ウレタンアクリレート、エステルアクリレート、エポキシアクリレート等の靱性付与を目的とするもの等を挙げることができ、これらは1種のみを単独で用いてもよいほか、2種以上を併用してもよい。この反応性希釈剤の配合割合は、通常、5～95重量%、好ましくは10～80重量%の範囲である。

【0032】また、ガラス基板との密着性を与えるシランカップリング剤としては、 $\gamma$ -（メタ）アクロイロキシプロピルトリメトキシシラン（ $\gamma$ -a Si）、 $\gamma$ -グリシロキシプロピルトリメトキシシラン（ $\gamma$ -Ep）、 $\gamma$ -メルカプトプロピルトリエトキシシラン、 $\gamma$ -アミノプロピルトリエトキシシラン等を挙げることができ、

を併用してもよい。これらのシランカップリング剤の配合割合は、重合性樹脂分総量に対して、通常、0.1～10重量%、好ましくは0.1～5重量%の範囲である。

【0033】更に、必要に応じて添加される粘性調整剤としての溶剤としては、エチルセロソルブアセテート(ECA)、プロピレングリコールモノメチルエーテルアセテート(PGMEA)、酢酸ブチル等のエステル系、シクロヘキサン、ジイソブチルケトン等のケトン系、ジエチレングリコールジメチルエーテル等のエーテル系、トルエン、キシレン等の芳香族炭化水素系、イソプロパノール等のアルコール系等のものを挙げることができ、これらは1種のみを単独で用いてもよいほか、2種以上を併用してもよい。この溶剤の配合割合は、重合性樹脂分100重量部に対して10～400重量部、好ましくは10～200重量部の範囲であり、この溶剤については、塗布後張り合わせ前に乾燥等により塗膜から除去しておくのが好ましい。

【0034】以上のようにして得られた透明プラスチック保護用コーティング材料、カラーフィルター用材料あるいは光学材料用接着剤には、実際に光学材料として使用する際にその耐候性や耐熱性の向上を目的として、紫外線吸収剤、光安定剤、酸化防止剤、熱重合防止剤等から選ばれた添加剤の1種又は2種以上が添加される。

【0035】この目的で使用される紫外線吸収剤としては、特に限定されるものではないが、本発明の光学材料用アクリレート樹脂組成物中に均一に分散し、耐候性を改良しクラックの発生を効果的に防止できるものであればよく、例えば、ベンゾフェノン系、ベンゾトリアゾール系、サリチル酸フェニル系、安息香酸フェニル系、シアノアクリレート系等から誘導される化合物で、その最大吸収波長が240～380nmの範囲にあるものが好適に使用される。

【0036】この紫外線吸収剤の具体例としては、2-ヒドロキシベンゾフェノン、5-クロロ-2-ヒドロキシベンゾフェノン、2,4-ジヒドロキシベンゾフェノン、2-ヒドロキシ-4-メトキシベンゾフェノン、2-ヒドロキシ-4-n-オクトキシベンゾフェノン、4-ドデシロキシ-2-ヒドロキシベンゾフェノン、2-ヒドロキシ-4-オクタデシロキシベンゾフェノン、2,2'-ジヒドロキシ-4-メトキシベンゾフェノン、2,2'-ジヒドロキシ-4,4'-ジメトキシベンゾフェノン、フェニルサリシレート、p-tert-ブチルフェニルサリシレート、p-81,1,3,3-テトラメチルブチルフェニルサリシレート、3-ヒドロキシフェニルベンゾエート、フェニレン-1,3-ジベンゾエート、2-(2-ヒドロキシ-5-メチルフェニル)ベンゾトリアゾール、2-(2-ヒドロキシ-5-tert-ブチルフェニル)-5-クロロベンゾトリ

ト-ブチルフェニル)ベンゾトリアゾール、2-(2-ヒドロキシ-5-tert-ブチルフェニル)ベンゾトリアゾール、2-(2-ヒドロキシ-4-オクチロキシフェニル)ベンゾトリアゾール等が挙げられ、これらは1種のみを単独で用いてもよいほか、2種以上を併用してもよい。この紫外線吸収剤の配合割合は、樹脂組成物の用途、膜厚、基板のフィルム等によっても異なるが、通常、1～20重量%、好ましくは2～15重量%の範囲である。

【0037】また、光安定剤としては、代表的には高分子用として用いられているヒンダードアミン系のもの、特に環状ヒンダードアミン構造を有するものを挙げることができ、具体的には、4-ベンゾイルオキシ-2,2,6,6-テトラメチルピペリジン、4-ヘキサノイルオキシ-2,2,6,6-テトラメチルピペリジン、4-オクタノイルオキシ-2,2,6,6-テトラメチルピペリジン、4-ステアロイルオキシ-2,2,6,6-テトラメチルピペリジン、コハク酸-ビス(2,2,6,6-テトラメチル-4-ピペリジル)、セバシン酸-ビス(2,2,6,6-テトラメチル-4-ピペリジル)、フタル酸-ビス(2,2,6,6-テトラメチル-4-ピペリジル)、トリメシン酸-トリス(2,2,6,6-テトラメチル-4-ピペリジル)等がある。これらは1種のみを単独で用いてもよいほか、2種以上を併用してもよい。この光安定剤の配合割合は、樹脂組成物の用途、膜厚、基板のフィルム等によっても異なるが、通常、1～20重量%、好ましくは2～10重量%の範囲である。

【0038】更に、加熱時の変色や熱重合を抑制する目的で添加される酸化防止剤や熱重合防止剤としては、公知のヒンダードフェノール系、チオエーテル系、有機リン系等の化合物が挙げられ、例えば、アデカアークス社製のイルガノックス1010のようなイルガノックスシリーズ、亜リン酸トリフェニル等が例示される。これら酸化防止剤や熱重合防止剤の配合割合は、樹脂組成物の用途、製造時の熱履歴等によっても異なるが、通常、0.01～10重量%、好ましくは0.01～2重量%の範囲である。

【0039】

【発明の実施の形態】9,9-ビス(4-ヒドロキシフェニル)フルオレンとエピクロロヒドリンとを塩基触媒の存在下に反応させてジグリシジルエーテル(エポキシ化合物)を合成し、このエポキシ化合物と(メタ)アクリル酸とを反応させ、色相APHA300以下のアクリレート樹脂からなる光学材料用アクリレート樹脂を得る。

【0040】このアクリレート樹脂に重合開始剤と必要に応じて添加される耐候性や耐熱性を改善するための添加剤やその他の添加剤を配合し、透明プラスチック保護

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ト樹脂に重合開始剤と必要に応じて添加される耐候性や耐熱性を改善するための添加剤や顔料等のその他の添加剤を配合し、カラーフィルター用材料を調製する。更に、上記アクリレート樹脂に重合開始剤と必要に応じて添加される耐候性や耐熱性を改善するための添加剤やその他の添加剤を配合し、光学材料用接着剤を調製する。

## 【0041】

【実施例】以下、実施例及び比較例に基づいて、本発明を具体的に説明する。なお、以下の実施例及び比較例で得られたアクリレート樹脂組成物について、色相APHAの測定は、測定対象物質の50重量%エチルセロソルブアセテート溶液を調製してJIS K-6901の規格に準じて行った。また、黄変度(YI)の測定は、標準C光源を使用した色度計(スガ試験機社製)を用い、透過光における3刺激値から $YI = (1.06X - 1.28Z) \div 100Y$ の式により求めた。

## 【0042】製造例1

エポキシ当量257及び色相APHA30の一般式

(2)で示されるエポキシ化合物75.0gと、アクリル酸20.1gと、2,6-ジ-tert-ブチル-4-ヒドロキシトルエン0.029gと、トリエチルベンジルアンモニウムクロライド0.13gとを還流冷却管付き500mlフラスコ中に仕込み、25ml/分の速度で乾燥空気を吹き込みながら100℃に加熱して均一な粘稠溶液を得た。

【0043】更に引き続き、116～118℃に加熱しながら攪拌を行い、随時エポキシ当量と酸価を測定して反応系外に飛散したアクリル酸約0.45gを補い、14時間後に色相APHA50の一般式(1)で示されるアクリレート樹脂(以下「FHPA」と略称する)を得た。

## 【0044】実施例1

上記製造例1で得られたFHPA5gに架橋剤としてジ\*

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\*ペンタエリスリトールヘキサアクリレート(DPHA、日本化薬社製)60g及び反応性希釈剤としてエチレングリコールジメタクリレート(EGDM、共栄社化学社製)35gを添加し、更に光重合開始剤として2-メチル-1-(4-メチルチオフェニル)-2-モルフォリノアロペン-1-オン(チバガイギー社製:イルガキュア-907)3gとを配合し、透明プラスチック保護用コーティング材料として組成Aのハードコート剤を調製した。

【0045】この組成Aのハードコート剤をポリカーボネート板上にスピンコーターにより塗布して7μmの厚さの塗膜を形成し、光照射して硬化膜とした後、250g/cm<sup>2</sup>の荷重、10往復のラビング条件で#0000のスチールウールテストを行った結果、全く傷が付かないという良好な結果が得られた。

【0046】また、この組成Aのハードコート剤をポリカーボネート板上にスピンコートを用いて塗布し、次いで光照射をして膜厚7μmの塗膜を形成し、得られた塗膜についてスガ試験機社製強エネルギーキセノンウエザーメーターSC700-WA型により耐候性試験を行った。この耐候性試験前後の黄変度及びクラック発生時間をそれぞれ測定した。結果は、耐候性試験前の黄変度(YI)が0.31で、600hr耐候性試験後の黄変度(YI)が0.8であって、クラック発生時間が750時間であった。

【0047】製造例2及び3並びに比較製造例1及び2表1に示すエポキシ当量及び色相APHAを有するエポキシ化合物を用い、製造例1と同様にして表1に示す色相APHAを有する製造例のFHPA及び比較製造例のCo-FHPAをそれぞれ調製した。

## 【0048】

## 【表1】

		原料エポキシ化合物の性状		生成物の略号と色相	
		色相(APHA)	エポキシ当量	略号	色相(APHA)
製造例	1	30	257	FHPA1	50
"	2	80	254	FHPA2	100
"	3	120	258	FHPA3	270
比較製造例	1	400	261	Co-FHPA1	400
"	2	500	247	Co-FHPA2	400

(注) FHPA: フォトリソグラフィ用アクリレート樹脂

## 【0049】実施例2～9及び比較例1～6

製造例1～3並びに比較製造例1及び2でそれぞれ得られたFHPA及びCo-FHPAを用い、添加剤として6官能性架橋剤のジペンタエリスリトールヘキサアクリレート(DPHA、日本化薬社製)、3官能性架橋剤の

※5、東亜合成社製)、反応性希釈剤のエチレングリコールジメタクリレート(EGDM、共栄社化学社製)、反応性希釈剤のイソボルニルアクリレート(IB-XA)、及び、光重合開始剤のイルガキュア-907を使用し、透明プラスチック保護用コーティング材料として

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これらの組成A～Cのハードコート剤はその何れも、チールールテストにおいて、数本から数十本の傷が入るといふ結果が得られた。

【0050】

【表2】

	ハードコート剤 組成 (g : 重量部)					
	FHPA	DPHA	EGDM	M315	IB-XA	Irg907
A	5	60	35	—	—	3
B	5	40	—	40	15	3
C	30	50	20	—	—	3

(注) FHPA: フォリントロキシプロピルアクリレート樹脂  
 DPHA: デンタリスプロピルアクリレート (日本化薬社製)  
 EGDM: エチレングリコールジメタクリレート (共栄社化学社製)  
 M315: トリス(アクロキシエチル)イソシアヌレート (東亜合成社製)  
 IB-XA: イソボルネンアクリレート (共栄社化学社製)  
 Irg907: イルガチアール-907 (チバガイヨー社製)

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\* 【0051】このようにして得られた各組成A～Cを有する各実施例2～9及び比較例1～6のハードコート剤について、上記実施例1と同様にして耐候性試験を行い、この耐候性試験前後の黄変度及びクラック発生時間をそれぞれ測定した。結果を上記実施例1の結果と共に表3に示す。

【0052】

【表3】

\*

		FHPA略号	ハードコート剤の組成	耐候性試験結果			
				試験前YI値	400hrs後YI値	600hrs後YI値	クラック発生時間(hr)
実施例	1	FHPA1	A	0.31		0.8	750
	2	"	B	0.4		0.9	1500
	3	"	C	0.9	1.5		650
	4	FHPA2	A	0.5		1.2	750
	5	"	B	0.58		1.4	1200
	6	"	C	1.2	1.7		600
	7	FHPA3	A	0.7		1.5	750
	8	"	B	0.7		1.7	1200
	9	"	C	1.5	2		600
比較例	1	Co-FHPA1	A	1		3.6	600
	2	"	B	1.1		4	900
	3	"	C	1.8	7		400
	4	Co-FHPA2	A	1.3		1*)	450
	5	"	B	1.4		6	800
	6	"	C	2	9		400

(注) YI値: 黄変度の値  
 \*): クラック発生時間測定値。

【0053】実施例10～17及び比較例7～10  
 上記製造例1及び3並びに比較製造例1で得られたFHPA1及び3並びにCo-FHPA1を用い、添加剤として反応性希釈剤の2-ヒドロキシエチルアクリレート(HEMA)、反応性希釈剤のトリエチレングリコールジアクリレート(3EGA)、3官能性架橋剤のトリス(アクロキシエチル)イソシアヌレート(M315、東亜合成社製)、ガラスとの密着性を与えるシランカップリング剤のγ-アクリロイロキシプロピルトリメトキシシ

※ア-907を使用し、光学材料用接着剤として表4に示す組成D～Gの接着剤を調製した。

【0054】

【表4】

	接着剤の組成 (g:重量部)					
	FHPA	HEMA	3EGA	M315	$\gamma$ -aSi	Irg907
D	66	33	—	—	9	3
E	50	50	—	—	7	3
F	25	—	75	—	3	3
G	30	40	—	30	7	3

(注) FHPA: 7オレシトキシプロピルアクリレート樹脂  
 HEMA: 2-ヒドロキシエチルアクリレート  
 3EGA: トリエチレングリコールアクリレート  
 M315: トリス(アクロキシエチル)イソシアヌレート (東亜合成社製)  
 $\gamma$ -aSi:  $\gamma$ -アクリロキシプロピルトリメトキシシラン  
 Irg907: イルガキア-907 (チバガイザー社製)

【0055】このようにして得られた各組成D～Gを有する各実施例10～17及び各比較例7～10の接着剤\*

		FHPA略号	接着剤の組成	耐候性試験結果			
				試験前YI値	200hrs後YI値	試験前接着強度	200hrs後接着強度
実施例	10	FHPA1	D	0.6	0.8	98	88
	11	"	E	0.41	0.61	93	85
	12	"	F	0.21	0.4	85	78
	13	"	G	0.6	0.9	100	88
	14	FHPA3	D	0.66	1.1	95	87
	15	"	E	0.52	0.84	92	86
	16	"	F	0.28	0.8	87	75
	17	"	G	0.65	1.2	95	85
比較例	7	Co-FHPA1	D	1.8	8	95	75
	8	"	E	1.2	6.8	87	75
	9	"	F	0.8	4	85	68
	10	"	G	1.3	8.5	92	70

(注) YI値: 黄変度の値  
 接着強度: kg/cm<sup>2</sup>

【0057】実施例18～23及び比較例11～14  
 上記各製造例並びに比較製造例で得られたFHPA1～3並びにCo-FHPA1、2を用い、添加剤として6官能性架橋剤のジペンタエリスリトールヘキサアクリレート (DPHA、日本化薬社製)、3官能性架橋剤のトリス (アクロキシエチル) イソシアヌレート (M315、東亜合成社製)、溶剤のエチルセロソルブアセテート (ECA)、ガラスとの密着性を与えるシランカップリング剤の $\gamma$ -アクリロキシプロピルトリメトキシシラン

\* について、各接着剤を2枚の厚さ5mmのガラス板の間に接着面積12.5mm×25mmで40 $\mu$ mの厚さとなるように塗布して挟み込み、高圧水銀灯 (400W) を用いて500mjの光を照射し、更に、100℃で2時間熱処理して接着させ、次いで強エネルギーキセノンサンシャインウエザーメーター (スガ試験機社製) を用いてブラックパネル温度63℃、降雨12分及び乾燥48分のサイクルで200時間放置する耐候性試験を行い、この耐候性試験の前後における接着初期の黄変度と接着強度 (23℃での引張剪断強度) と耐候性試験200時間後の黄変度と接着強度とを調べた。結果を表5に示す。

【0056】

【表5】

※ラン ( $\gamma$ -aSi)、増感剤のミヒラーケトン (MK)、及び、光重合開始剤のイルガキュア-907を使用し、カラーフィルター用保護膜剤として表6に示す組成H及びIの保護膜剤を調製した。なお、これらの保護膜剤は、0.2ミクロンテフロンフィルターを用いて0.2kg/cm<sup>2</sup>の圧力で加圧濾過されたものである。

【0058】

【表6】

	カラーフィルタ用保護膜剤の組成 (g:重量部)						
	FHPA	DPHA	M315	ECA	$\gamma$ -aSi	MK	Irg907
H	70	30	—	240	3	1	3
I	70	30	10	250	3	1	3

(注) FHPA: フォトリソグラフィ用アクリレート樹脂  
 DPHA: ジペンタエリスリトールヘキサアクリレート (日本化薬社製)  
 M315: トリス(アクリロキシエチル)イソシアヌレート (東亜合成社製)  
 ECA: エチルセロソルファテート  
 $\gamma$ -aSi:  $\gamma$ -アクリロキシプロピルトリメトキシシラン  
 MK: ミラネトン  
 Irg907: イルギンア-907 (チバガイギー社製)

【0059】このようにして得られた各実施例及び各比較例の保護膜剤をSiO<sub>2</sub>コーティングしたガラス基板上にスピンコートにて塗布し、80℃で3分間乾燥し、次いで得られた塗膜を365nmの光で200mjの露光を行い、続いて200℃で1時間の熱処理をした。得られた塗膜は膜厚2μmで非常に均一であり、ゲル状物は観察されなかった。

【0060】得られた各実施例及び各比較例の塗膜について、クリーンオープン中250℃で1時間の熱処理を行う耐熱性試験を行い、この耐熱性試験の前後における黄変度を測定して比較した。結果を表7に示す。

【0061】

【表7】

		FHPA略号	保護膜 剤の組 成	耐熱性試験結果	
				試験前YI値	試験後YI値
実 施 例	18	FHPA1	H	0.1	0.8
	19	"	I	0.1	0.9
	20	FHPA2	H	0.2	1.2
	21	"	I	0.2	1.2
	22	FHPA3	H	0.4	1.9
	23	"	I	0.4	1.5
比 較 例	11	Co-FHPA1	H	1.5	4.9
	12	"	I	1.8	4.3
	13	Co-FHPA2	H	1.8	5.2
	14	"	I	1.9	4.2

(注) YI値: 黄変度の値

\*【0062】

【発明の効果】本発明の光学材料用アクリレート樹脂組成物は、耐候性試験時や耐熱性試験時における黄変が少なく、これによって安定剤等の添加剤を添加する量的自由度が増し、また、同じ添加量であれば硬化膜の黄変の程度を低減でき、しかも、クラックの発生も可及的に防止できる。このため、透明プラスチック保護用コーティング材料、カラーフィルター用材料、光学材料用接着剤等の光学材料の用途に好適に用いることができる。

フロントページの続き

(72)発明者 寺本 武郎  
 神奈川県川崎市中原区井田1618番地、新日本製鐵株式会社技術開発本部内

(72)発明者 白石 和人  
 神奈川県川崎市麻生区千代ヶ丘1-3-1

## \* NOTICES \*

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] When this invention forms a paint film, it relates to the optical material using the acrylate resin for optical materials and this which have the performance which it not only excels in transparency, but was excellent in hardness, weatherability, thermal resistance, adhesion, etc.

[0002]

[Description of the Prior Art] The coating material for protection and optical adhesives which protect the front face of transparent plastics optical materials, such as a lens, Light Emitting Diode, a plastics film, a substrate, and an optical disk, conventionally, furthermore, as what forms the hardening layer of optical materials, such as light filters, such as a LCD and an image pick-up element, or an electronic material using the acrylate resin which makes a fluorene hydroxy propylacrylate resin a principal component is proposed (JP,3-106918,A --) JP,3-205417,A, JP,5-194338,A, JP,4-351674,A, JP,4-345608,A, JP,4-337307,A.

[0003] It has the performance in which the hardening layer which this acrylate resin makes harden this and is obtained is not only excellent in thermal resistance or moisture resistance, but was excellent in the adhesion to substrates, such as a low hardening contraction, a pencil degree of hardness, chemical resistance, electrolytic-etching-proof nature, an electric insulation, abrasion-proof nature, and glass, etc., and the application for intended use, such as a protective coat extensively used in an optical material, an electronic material, etc., is expected.

[0004] however, this acrylate resin as the coating material for protection and optical adhesives which protect the front face of optical materials, such as a lens, Light Emitting Diode, and an optical disk Or if additives, such as an ultraviolet ray absorbent, a light stabilizer, an antioxidant, and a thermal polymerization inhibitor, are added weatherability and for the purpose of heat-resistant enhancement when using for intended use, such as a light filter The hardening layer formed at the time of a weathering test and a heat-resistant examination may yellow, and it may be unable to be used as the coating material for these protection, or the adhesives for optical materials or the charge of light-filter material. Moreover, if the addition of these additives is lessened in order to prevent occurrence of this problem beforehand, the problem that neither weatherability nor thermal resistance is necessarily enough will remain.

[0005]

[Problem(s) to be Solved by the Invention] Then, this invention persons prevent the problem of yellowing of the hardening layer produced when additives, such as a stabilizer, are added as much as possible. The result zealously examined about the acrylate resin for optical materials which can employ efficiently the property which an acrylate resin has by this in the maximum, By suppressing the hue of a fluorene hydroxy propylacrylate resin to 300 or less APHA The increase of quantitative degree of freedom to which there is little yellowing at the time of a weathering test and a heat-resistant examination, and it adds additives, such as a stabilizer, by this, Moreover, when it was the same

addition, the grade of yellowing of a hardening layer could be reduced, and it found out that the acrylate resin for optical materials which can also prevent occurrence of a crack as much as possible was moreover obtained, and this invention was completed.

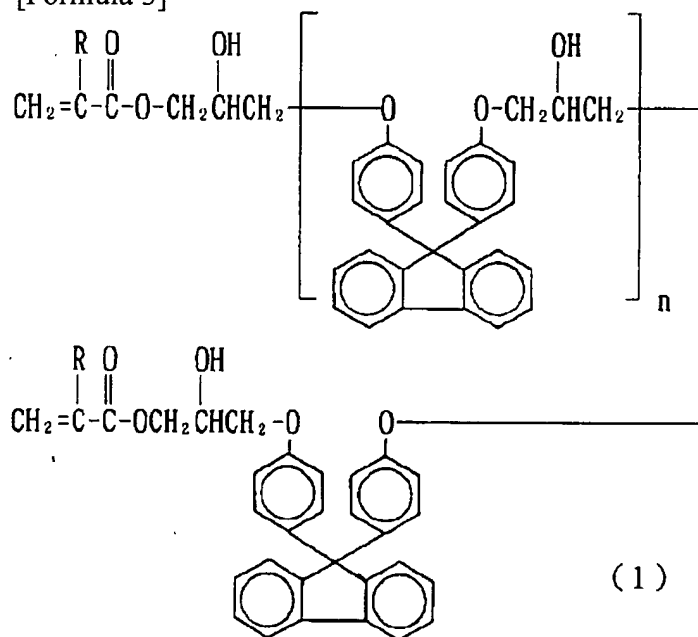
[0006] Therefore, the purpose of this invention has little yellowing at the time of a weathering test and a heat-resistant examination, if the quantitative degree of freedom which adds additives, such as a stabilizer, by this is increase and the same addition, it can reduce the grade of yellowing of a hardening layer, and it is to offer the acrylate resin for optical materials which can also prevent occurrence of a crack as much as possible moreover.

[0007] Moreover, other purposes of this invention are to offer the coating material for transparent plastics protection and the charge of light-filter material which used such an acrylate resin for optical materials, and the adhesives for optical materials.

[0008]

[Means for Solving the Problem] That is, this invention is the following general formula (1).

[Formula 3]



It is the acrylate resin for optical materials which consists of a 300 or less hue APHA [ which is expressed with (however, R in a formula shows either a hydrogen atom or a methyl group, and n is the integer of 0-20) ] acrylate resin.

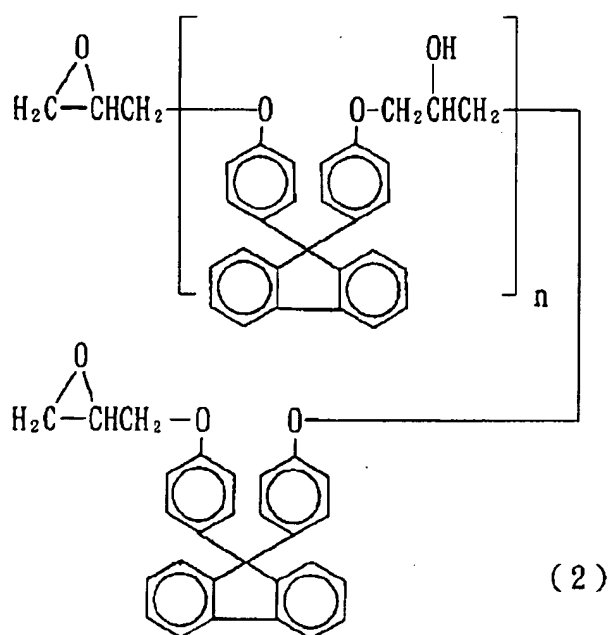
[0009] Moreover, this invention is the coating material for transparent plastics protection and the charge of light-filter material which used such an acrylate resin for optical materials, or the adhesives for optical materials.

[0010] In this invention, a 300 or less hue APHA [ which is expressed with a general formula (1) ] acrylate resin (it may only be hereafter called a "raw material resin") is manufactured as follows. First, 9 and 9-screw (4-hydroxyphenyl) fluorene and epichlorohydrin are made to react to the bottom of presence of a base catalyst, and it is the following formula (2).

[0011]

[Formula 4]





The diglycidyl ether (a "epoxy compound" is only called hereafter) expressed with (however,  $n$  in a formula is the integer of 0-20) is compounded. By changing the reaction mole ratio of 9 and 9-screw (4-hydroxyphenyl) fluorene and epichlorohydrin in the case of this reaction, several  $n$  can be controlled repeatedly and the value which is this  $n$  [ several ] repeat can be calculated by GPC measurement.

[0012] Next, the epoxy compound and the following general formula (3) of a formula (2) which do in this way and were obtained

[Formula 5]

✖ ID=000006

The acrylic acid expressed with (however,  $R$  in a formula shows either a hydrogen atom or a methyl group) (meta) is made to react, and the raw material resin of a general formula (1) is obtained. Here, in order to obtain the raw material resin of a 300 or less-APHA hue, in the reaction of the epoxy compound of a formula (2), and the acrylic acid (meta) of a general formula (3), it is good to satisfy the following conditions.

[0013] First, it is necessary to use the thing of a 300 or less-APHA hue at least, and the thing of a 200 or less-APHA hue is preferably used about the epoxy compound of a formula (2). If the hue of the epoxy compound of this formula (2) exceeds APHA300, it will become difficult to make hue APHA of the raw material resin generated or less into 300. Moreover, if the hue of the epoxy compound of this formula (2) is 200 or less APHA, reaction temperature and the degree of option about reaction time will increase.

[0014] Moreover, an acrylic acid (meta) is made to react at a rate of the 90 - 102 equivalent preferably the 90 to 110 equivalent to the epoxy-compound 100 equivalent in the reaction of the epoxy compound of a formula (2), and the acrylic acid (meta) of a general formula (3). (Meta) If it falls, and the crosslinking density at the time of optical hardening when using this thing as a coating agent when there was less amount of the acrylic acid used than the 90 equivalents is not desirable and increases more than the 110 equivalent, an unreacted (meta) acrylic acid will remain and weatherability will fall as a coating layer.

[0015] In the case of this reaction, as occasion demands And 2, 6-G t-butyl-4-hydroxytoluene, Polymerization inhibitors, such as the hydroquinone monomethyl ether, t-butyl catechol, and a phenothiazin Triethyl benzyl ammoniumchloride, a triethylamine, a benzyl dimethylamine, Methyl triethyl ammoniumchloride, a triphenyl phosphine, The catalyst of a tetraethylammonium star's picture

etc., and the methyl-cellosolve acetate added if needed for viscous adjustment, Ethylcellosolve acetate, butyl-cellosolve acetate, diethylene-glycol-monoethyl-ether acetate, The solvent with the boiling point more than reaction temperature, such as diethylene-glycol wood-ether acetate, propylene-glycol-monomethyl-ether acetate, and gamma-butyrolactone, is added.

[0016] Here, the amount of the polymerization inhibitor used is less than 0.5 % of the weight preferably 1 or less % of the weight to reaction raw material mixture, the amount of the catalyst used is 0.001 - 3 % of the weight preferably 0.001 to 5% of the weight to reaction raw material mixture, and the amount of the solvent used is 5 - 200 % of the weight preferably five to 500% of the weight to reaction raw material mixture. If the amount of the polymerization inhibitor used exceeds 1 % of the weight, when it uses as a coating agent, the crosslinking density of the paint film at the time of hardening will not go up, but problems, such as a shortage of a degree of hardness and poor adhesion, will arise. Moreover, if the amount of the catalyst used is less than 0.001 % of the weight, the problem that a gelation object is generated in the system of reaction will arise. Furthermore, although it is effective in the viscous fall at the time of a reaction, if 500 % of the weight is exceeded and it adds, it becomes long and is not desirable [ adding a solvent 5% of the weight or more / reaction time ].

[0017] Moreover, 90-130 degrees C of reaction temperature are usually 95-125 degrees C preferably, and the reaction time of the reaction condition of these epoxy compounds and an acrylic acid (meta) is usually 4 - 18 hours preferably for 3 to 24 hours. If it will be necessary to use the epoxy resin of a 200 or less hue APHA formula (2) at least in order to obtain a 300 or less hue APHA raw material resin, if reaction temperature exceeds 130 degrees C and/or reaction time exceeds 24 hours, reaction time will become extremely long too much on the contrary if reaction temperature is less than 90 degrees C, and reaction time is less than 3 hours, it will be necessary to make reaction temperature high, and is not desirable. Furthermore, it is good to carry out, usually blowing a dry air into the system of reaction, in order to suppress the polymerization of the double bond section.

[0018] By the way, in order for a hue to obtain the epoxy compound of the formula (2) which is 200 or less APHA preferably 300 or less APHA, a hue needs to use a 200 or less-APHA thing about the screw (hydroxyphenyl) fluorene which is the manufacture raw material. If the hue of the screw (hydroxyphenyl) fluorene of this manufacture raw material exceeds APHA200, it will become difficult to obtain a 300 or less hue APHA epoxy compound. in addition, the full which is a kind of the manufacture raw material in order to obtain a 200 or less hue APHA [ such ] screw (hydroxyphenyl) fluorene -- me -- non, it is necessary to use the bisphenol refined and recrystallized using what was alike, stuck, carried out distillation refining, and made the alkali of an oxidation catalyst, and the content of heavy metal less than 1 % of the weight \*\*\*\*, or as a bisphenol of a manufacture raw material

[0019] Furthermore, 300 or less hue APHA, in order to obtain the epoxy compound of a 200 or less-APHA formula (2) preferably It is necessary to stop the residual fluorene in the screw (hydroxyphenyl) fluorene of a manufacture raw material to less than 1% of the weight and also, and The inside of the system of reaction is replaced by inert gas, such as nitrogen, in the case of a glycidyl ether-ized reaction. remove oxygen or It is good to perform elimination operation of residual epichlorohydrin performed after a glycidyl ether-ized reaction below 150 degrees C, or to perform temperature in the case of desolventization-izing of a culmination below 180 degrees C further.

[0020] Thus, the adhesives for the coating material for transparent plastics protection, the charge of light-filter material, or optical materials explained below are prepared by blending a polymerization initiator with the acrylate resin for optical materials which consists of a 300 or less hue APHA [ which was obtained ] fluorene hydroxy propylacrylate resin at least.

[0021] First, about the coating material for transparent plastics protection, a polymerization initiator is blended with the acrylate resin for optical materials of the above-mentioned this invention as an indispensable component, and the reactant diluent for the cross linking agent for degree-of-hardness grant or the enhancement in adhesion and viscosity control, a leveling agent, etc. are added further if needed.

[0022] Here, a photopolymerization initiator and a thermal polymerization initiator are mentioned as a polymerization initiator used when preparing such a coating material for transparent plastics protection.

As a photopolymerization initiator, specifically A benzophenone, 2, and 2-dimethoxy-2-phenyl acetophenone, A 2 and 2-diethoxy-2-phenyl acetophenone, 2-ethyl anthraquinone, 2, 4-diethyl thioxan ton, a diisopropyl thioxan ton, A benzyl dimethyl ketal, a 2-hydroxy cyclohexyl phenyl ketone, 2-hydroxy -2-methyl-1-phenyl propane-1-ON, 2-methyl-1-[- (methylthio) 4 Phenyl]-2-morpholino-propane-1-ON, etc. are mentioned.

[0023] As a thermal polymerization initiator, a well-known peroxide system initiator and an azobis system initiator can be used. moreover, as a peroxide system initiator Specifically Methyl ethyl ketone peroxide, methyl-isobutyl-ketone peroxide, Cyclohexanon peroxide, methylcyclohexane ketone peroxide, The thing of ketone peroxide systems, such as acetylacetone peroxide Isobutyl peroxide, m-\*\*\*\*\* benzoyl peroxide, 2, 4-dichlorobenzoyl peroxide, alpha-methyl benzoyl peroxide, Screw - The thing of diacyl peroxide systems, such as 3, 5, and 5-trimethylhexanoyl peroxide 2, 4, and 4-trimethyl pentyl-2-hydroperoxide, diisopropylbenzene hydroperoxide, The thing of hydroperoxide systems, such as a cumene hydroperoxide and t-butyl hydroperoxide Dicumyl peroxide, 2, the 5-dimethyl -2, 5-di-tert-butyl peroxide hexane, The thing of dialkyl peroxide systems, such as 1, 3-screw (t-butyl \*\*\*\*\* seesaw propyl) benzene, and t-butyl cumyl peroxide 1 and 1-G tert-butyl peroxide - 3, 3, a 5-trimethyl cyclohexane, The thing of peroxy ketal systems, such as 2 and 2-G (tert-butyl peroxide) butane, 4, and 4-G tert-butyl peroxide valeric-acid-n-butyl ester 2, 4, and 4-\*\*\*\*\* peroxy phenoxy acetate, Alpha-cumilperoxy neodecanoate, t-butyl par oxybenzoate, The thing of alkyl par ester systems, such as a G t-butyl par \*\*\*\*\* peat G t-\*\*\*\*\* butylperoxy dicarbonate, di-2-ethylhexylperoxycarbonate, Screw (4-t-butyl cyclohexyl) peroxi dicarbonate, The thing of par carbonate systems, such as diisopropyl peroxi dicarbonate Things, such as other acetyl cyclohexyl sulfonyl peroxi dicarbonate and t-butyl \*\*\*\*\* sialyl carbonate, are mentioned. as an azobis system initiator Specifically A 1 and 1'-azobis cyclohexane-1-carbonitrile, - azobis - (2,4-dimethylvaleronitrile), and 2 and 2'2, 2'-azobis - (4-methoxy-2,4-dimethylvaleronitrile), - azobis - (isobutyronitrile), and 2 and 2'-azobis - (methyl iso butyrate), alpha, and alpha'4, 4'-azobis - (4-cyano \*\*\*\*\* acid) etc. is mentioned.

[0024] The either can be independently used for these photopolymerization initiators or a thermal polymerization initiator, and also they can also be used as two or more sorts of mixture. the amount used As opposed to total section of 100 weight of the acrylate resin for optical materials shown by the general formula (1) and the polyfunctional acrylate compound of polymerization nature mentioned later, and a reactant diluent the former photopolymerization initiator -- 0.1 - 30 weight section -- it is below 20 weight section preferably, and the latter thermal polymerization initiator is 0.1 - 10 weight section There is a possibility that a rate of polymerization may become slow and it may become insufficient hardening it if a combination domain is less than this domain, and on the contrary, if it exceeds this domain, it will become the cause of the adhesion fall to the shortage of thermal resistance and substratum by molecular weight fall of a hardened material.

[0025] moreover, about the cross linking agent added if needed Tris (\*\*\*\*\* ethyl) isocyanurate (\*\*\*\* synthesis company make : M315), \*\*\*\*\* ERIS \*\*\*\*\* (meta) acrylate, dipentaerythritol tetrapod (meta) acrylate, Dipentaerythritol \*\*\*\*\* (meta) acrylate, dipentaerythritol hexa (meta) acrylate, \*\*\*\*\* ERIS \*\*\*\*\* (meta) acrylate, tripentaerythritol tetrapod (meta) acrylate, 3 functionality cross linking agents, such as tripentaerythritol \*\*\*\*\* (meta) acrylate and tripentaerythritol hexa (meta) acrylate, are mentioned, these may use only one sort independently, and also they may use two or more sorts together. Although the blending ratio of coal of this cross linking agent is based on the performances made into the purpose, such as intended use and a degree of hardness, it is usually 20 - 90 % of the weight among the polymerization nature resinous principles in a resin constituent (a content, a bulking agent, a solvent, and a polymerization initiator are removed).

[0026] Furthermore, about the reactant diluent added if needed, ethylene glycol dimethacrylate (EGDM), isobornyl acrylate (:IB[ by the Kyoeisha chemistry company ]- XA), N-vinyl pyrrolidone, tetrahydrofurfuryl acrylate (:THF[ by the Kyoeisha chemistry company ]-A), caprolactone denaturation tetrahydrofurfuryl acrylate, etc. are mentioned, these may use only one sort independently, and also they may use two or more sorts together, for example. Although the blending ratio of coal of this reactant diluent is based on the proper viscosity by the applying method, it is used at less than 80 % of the weight

in a polymerization nature resinous principle.

[0027] It is useful for the intended use of transparent plastics optical materials, such as a lens, Light Emitting Diode, a plastics film, a substrate, and an optical disk, for example, applies to a front face by the spin coat method, and using a hot plate, oven, an infrared heating furnace, etc., it heats, and it is stiffened [ using low voltage or a high pressure mercury vapor lamp, a xenon LGT, etc. the coating material for transparent plastics protection of this invention irradiates ultraviolet rays, stiffens them, or ], and makes a coating layer form in front faces, such as

[0028] Moreover, about the charge of light-filter material, the polymerization initiator same as an indispensable component as the above is blended with the acrylate resin for optical materials of the above-mentioned this invention. The need is embraced. Furthermore, an anthraquinone system pigment, a perylene system pigment, a \*\*\*\*\* system pigment, An iso indoline system pigment, a halogenation phthalocyanine system pigment, carbon, Pigments, such as titanium carbon and an iron oxide, and a phenol novolak type epoxy resin, A cresol novolak type epoxy resin, a tris phenol methane system epoxy resin, Other epoxy resins, such as a bisphenol A type epoxy resin and a bisphenol female mold epoxy resin Furthermore, the epoxy (meta) acrylate which these epoxy resins and an acrylic acid (meta) are made to react, and is obtained, Macromolecule unsaturation machine inclusion resins, such as a resultant which this epoxy (meta) acrylate, the aforementioned polybasicity carboxylic acid, or its anhydride is made to react, and is obtained 2-hydroxyethyl (meta) acrylate, benzyl acrylate, Dipentaerythritol hexaacrylate, \*\*\*\*\* roll pro pantry (meta) acrylate, The single organic functions and polyfunctional (meta) acrylic esters in which a polymerization is possible, such as pen \*\*\*\*\* (meta) acrylate and diethylene-glycol (meta) acrylate 2-methyl mentioned above - Photopolymerization initiators, such as 1-[- (methylthio) 4 Phenyl]-2-morpholino propane-1-ON Peroxides, such as isobutyl peroxide, N and N-dimethylamino ethyl-benzoate ester, Photosensitizers, such as N and N-dimethylamino isoamyl-benzoate ester, a triethanolamine, and a triethylamine, and the additive for light filters with a silane coupling agent, a light stabilizer, an antioxidant, etc. well-known in addition to this are added.

[0029] The charge of light-filter material of this invention can be used as a resin constituent for the protective coats of a light filter, without adding a pigment, and also it can add a pigment and it can also be used for it as ink of a light filter. And the resin constituent for protective coats and ink for these light filters can be used conventionally like the well-known resin constituent for protective coats and well-known ink, and can form a protective coat and a detailed pattern excellent in thermal resistance and flat nature.

[0030] Furthermore, about the adhesives for optical materials, the solvent for the silane coupling agent which gives the adhesion with the reactant diluent and glass substrate which add the polymerization initiator same as an indispensable component as the above, and give adhesion and toughness further if needed at the acrylate resin for optical materials of this invention, and viscosity control, a sensitizer, etc. are added.

[0031] As a reactant diluent added in these adhesives for optical materials if needed 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), Tetrahydrofurfuryl (meta) acrylate, isobornyl (meta) acrylate, The thing aiming at adhesion grant and viscous adjustment of N-vinyl pyrrolidone etc., The thing aiming at toughness grant of triethylene glycol diacrylate (3EGA), urethane acrylate, ester acrylate, epoxy acrylate, etc. can be mentioned, these may use only one sort independently, and also they may use two or more sorts together. The blending ratio of coal of this reactant diluent is usually 10 - 80% of the weight of a domain preferably five to 95% of the weight.

[0032] Moreover, as a silane coupling agent which gives the adhesion with a glass substrate, gamma-(meta) \*\*\*\*\* yloxy propyl trimethoxysilane (gamma-aSi), gamma-\*\*\*\*\* propyl trimethoxysilane (gamma-Ep), gamma-mercapto propyl triethoxysilane, gamma-aminopropyl triethoxysilane, etc. can be mentioned, these may use only one sort independently, and also they may use two or more sorts together. The blending ratio of coal of these silane coupling agents is usually 0.1 - 5% of the weight of a domain preferably 0.1 to 10% of the weight to a polymerization nature pitch total amount.

[0033] furthermore, as a solvent as a viscous regulator added if needed

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Since it became timeout time, translation result display processing is stopped.

## \* NOTICES \*

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2. \*\*\*\* shows the word which can not be translated.

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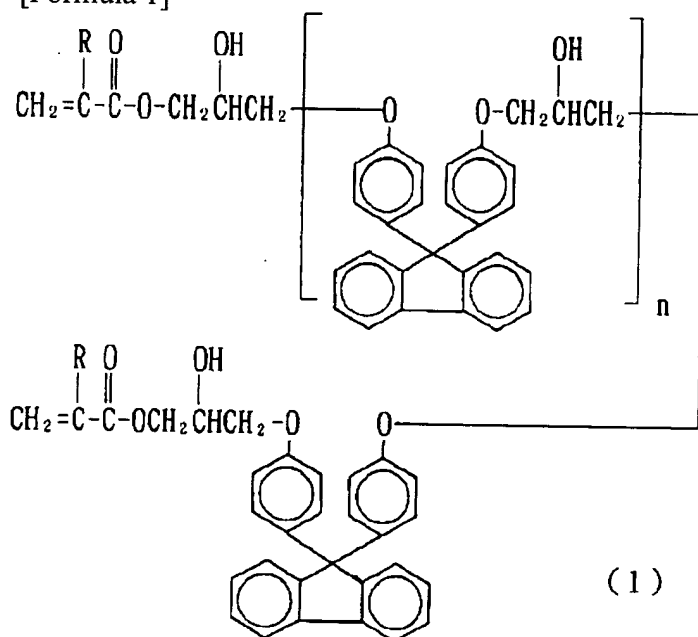
 CLAIMS
 

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[Claim(s)]

[Claim 1] The following general formula (1)

[Formula 1]

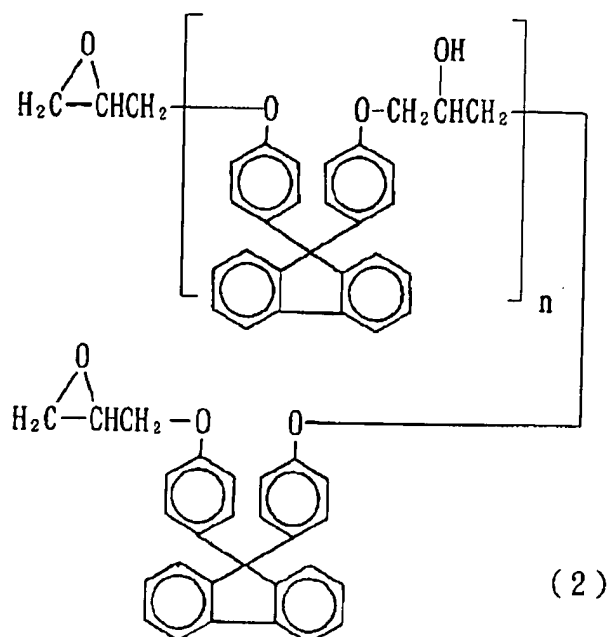


It is the acrylate resin for optical materials characterized by consisting of a 300 or less hue APHA [ which is expressed with (however, R in a formula shows either a hydrogen atom or a methyl group, and n is the integer of 0-20) ] acrylate resin.

[Claim 2] An acrylate resin is the 200 or less hue APHA following general formula (2).

[Formula 2]

*Fluorene*



It is the acrylate resin for optical materials according to claim 1 which the diglycidyl ether and the acrylic acid (meta) which are expressed with (however, n in a formula is the integer of 0-20) are made to react, and is obtained.

[Claim 3] The coating material for transparent plastics protection characterized by including the acrylate resin for optical materials and a polymerization initiator according to claim 1 or 2 as an indispensable component.

[Claim 4] The charge of light-filter material characterized by including a pigment as an indispensable component if needed, including the acrylate resin for optical materials and a polymerization initiator according to claim 1 or 2.

[Claim 5] Adhesives for optical materials characterized by including the acrylate resin for optical materials and a polymerization initiator according to claim 1 or 2 as an indispensable component.

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[Translation done.]

PTO 02-2330

Japanese Kokai Patent Application  
No. Hei 9[1997]-241340

ACRYLATE RESIN FOR OPTICAL MATERIAL AND OPTICAL  
MATERIAL MADE OF SAME

Hironobu Kawasato, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C. APRIL 2002  
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KOKAI PATENT APPLICATION NO. HEI 9[1997]-241340

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Examination Request:	Not filed

ACRYLATE RESIN FOR OPTICAL MATERIAL AND OPTICAL MATERIAL MADE OF  
SAME

[Kogaku zairyoyo akurireto jushi oyobi koreo mochiita kogaku zairyo]

Inventors:	Hironobu Kawasato, et al.
Applicant:	000006644 Nippon Steel Chemical Co., Ltd., and 000006644 Nippon Steel Corporation

[There are no amendments to this patent.]

\* \* \*

Claims

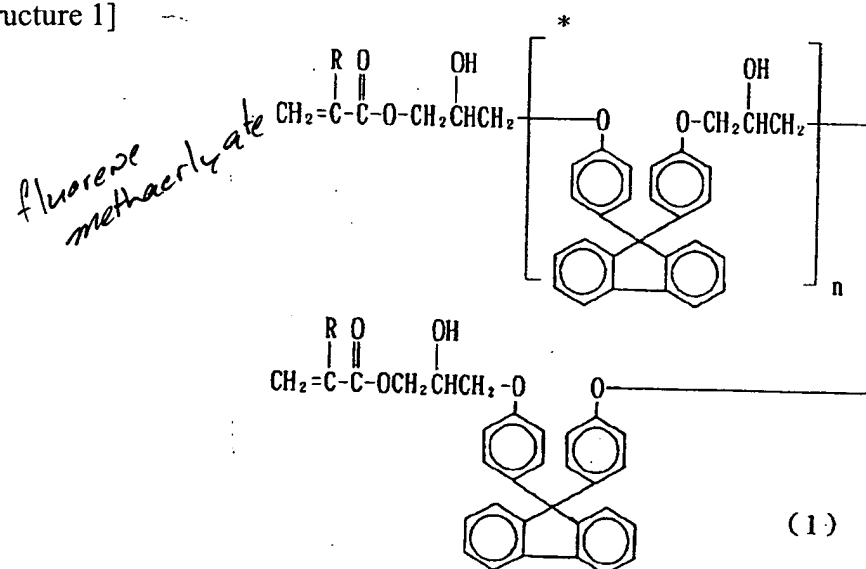
/2\*

1. A type of acrylate resin for optical material characterized by the fact that it is made of  
acrylate resin represented by the following formula (1):

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\* [Numbers in the margin indicate pagination in the foreign text.]

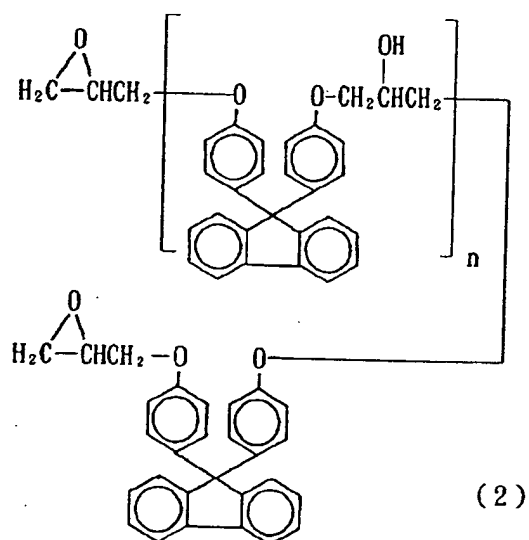
[Structure 1]



(Where R represents an hydrogen atom or methyl group, and n is an integer in the range of 0-20) and having hue APHA of 300 or lower.

2. The acrylate resin for optical material described in Claim 1, characterized by the fact that the acrylate resin having hue APHA of 200 or less is prepared in a reaction between diglycidyl ether represented by the following formula (2)

[Structure 2]



(Where n is an integer in the range of 0-20) and (meth)acrylic acid.

3. A type of coating material for protecting transparent plastics characterized by the fact that it contains as necessary components the acrylate resin for optical material described in Claim 1 or 2, and a polymerization initiator.

4. A type of material for color filter characterized by the fact that it contains as necessary components the acrylate resin represented in Claim 1 or 2 and a polymerization initiator, and, as needed, it also contains a pigment.

5. A type of adhesive for optical material characterized by the fact that it contains as necessary components the acrylate resin described in Claim 1 or 2 and a polymerization initiator.

### Detailed explanation of the invention

[0001]

#### Technical field of the invention

This invention pertains to a type of acrylate resin for optical material, which not only has excellent transparency when a coating film is formed, but also has excellent properties, such as hardness, weatherability, heat resistance, adhesion property, etc., and a type of optical material made of said acrylate resin.

[0002]

#### Prior art

In the prior art, acrylate resins mainly made of fluorene hydroxypropyl acrylate resin have been proposed as protective coating materials for protecting surfaces of lenses, LED, plastic films, substrates, optical disks, and other transparent plastic optical materials, or as an optical adhesive, or for forming cured films as color filters for liquid crystal display devices, image pickup elements, etc., and other electronic materials (see: Japanese Kokai Patent Application Nos. Hei 3[1991]-106918, Hei 3[1991]-205417, Hei 5[1993]-194338, Hei 4[1992]-351674, Hei 4[1992]-345608, and Hei 4[1992]-337307).

[0003]

Said acrylate resin has excellent properties. For the cured films prepared from it, not only are the heat resistance and moisture resistance high, but they also have low curing shrinkage, pencil hardness, chemical resistance, electrolysis corrosion resistance, electrical insulating property, scratch resistance, and adhesion to glass or other substrate. Said resin is thus expected to find use in making protective films, etc., widely used in optical materials and electronic materials.

[0004]

However, the acrylate resin has some problems. In order to improve the weatherability and heat resistance when the acrylate resin is used as a protective coating material for protecting surfaces of lenses, LED, optical disks, and other optical materials, or as an optical adhesive, or for forming color filters, etc., a UV absorbent, optical stabilizer, oxidation inhibitor, thermal polymerization inhibitor, and other additives are added. In this case, yellowing occurs in the cured films formed and used in weatherability tests and heat resistance tests, so that it may be impossible to use them as protective coating materials, adhesive of optical materials, or color filters. When the amounts of said additives are reduced to prevent said problem, weatherability and heat resistance may become insufficient. This is also undesired.

[0005]

Problems to be solved by the invention

In order to solve the aforementioned problems, the present inventors have performed extensive research on development of acrylate resin for optical material that can prevent as much as possible the problem of yellowing of the cured film that would otherwise take place when a stabilizer and other additives are added, so that the characteristics of the acrylate resin can be fully displayed. As a result of this research, it was found that when the hue APHA of fluorenehydroxypropyl acrylate resin is controlled to 300 or lower, yellowing during tests of weatherability and heat resistance becomes less significant. As a result, the freedom of choice of the amounts of stabilizer and other additives is increased, and the degree of yellowing of the cured film can be reduced for the same amounts of addition. Also, formation of cracks can be prevented for the obtained acrylate resin for optical material. As a result, this invention was reached.

[0006]

Consequently, the purpose of this invention is to provide a type of acrylate resin for optical material, for which yellowing during tests of weatherability and heat resistance becomes less significant, the freedom of choice the amounts of stabilizer and other additives is increased, the degree of yellowing of the cured film can be reduced for the same amounts of addition, and formation of cracks can be prevented.

[0007]

Another purpose of this invention is to provide a type of coating material that makes use of said acrylate resin for optical material and acts to protect transparent plastics, as well as a type of material for color filters, and a type of adhesive for optical material.

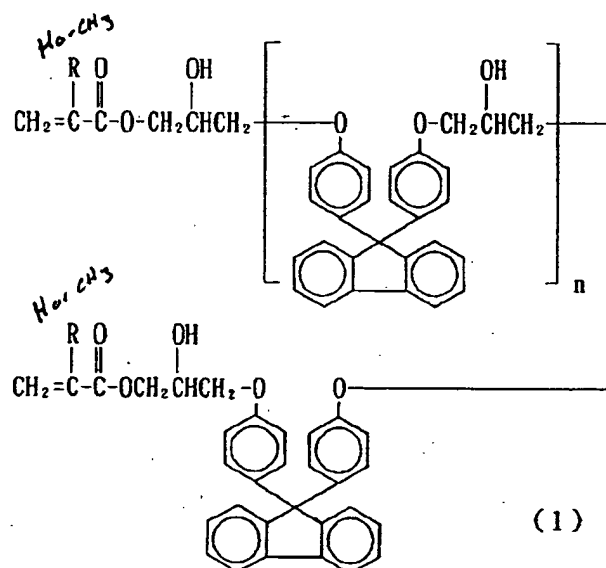
[0008]

Means to solve the problems

That is, this invention provides a type of acrylate resin for optical material characterized by the fact that it is made of an acrylate resin represented by the following formula (1):

[Structure 3]

*Fluorene methacrylate.*



(Where R represents a hydrogen atom or methyl group, and n is an integer in the range of 0-20) and having hue APHA of 300 or lower.

[0009]

Also, this invention provides a type of coating material for protecting transparent plastics, a type of material for color filters, and a type of adhesive for optical material, which are made of said acrylate resin for optical material.

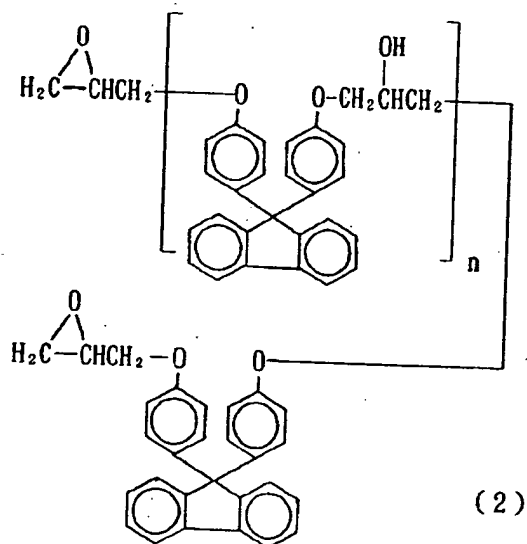
[0010]

According to this invention, the acrylate resin represented by formula (1) and having hue APHA of 300 or lower (hereinafter referred to as "feed resin") is prepared as follows: first of all, in the presence of a basic catalyst, a reaction is performed between 9,9-bis(4-hydroxyphenyl)fluorene and epichlorohydrin to form diglycidyl ether (hereinafter referred to as "epoxy compound") represented by the following formula (2):

[0011]

[Structure 4]

/4



(Where n is an integer in the range of 0-20).

During this reaction, n can be controlled by changing the reaction molar ratio of 9,9-bis(4-hydroxyphenyl)fluorene to epichlorohydrin. The value of said repeating number n can be determined by GPC measurement.

[0012]

Then, the epoxy compound represented by formula (2) obtained above is reacted with (meth)acrylic acid represented by formula (3):

[Structure 5]



(Where R represents a hydrogen atom or methyl group) to form the feed resin represented by formula (1). In this case, in order to obtain the feed resin with hue APHA of 300 or lower, in the reaction between the epoxy compound represented by formula (2) and (meth)acrylic acid represented by formula (3), the following condition should be met.

[0013]

First of all, for the epoxy compound represented by formula (2), it is necessary for it to have hue APHA of 300 or lower, or preferably 200 or lower. If the hue APHA of the epoxy compound represented by formula (2) is over 300, it is difficult to have the hue APHA of 300 or lower in the feed resin formed. Also, when the hue APHA of the epoxy compound represented by formula (2) is 200 or lower, it is possible to increase the freedom of choice in selecting the reaction temperature and reaction time.

[0014]

In the reaction between the epoxy compound represented by formula (2) and (meth)acrylic acid represented by formula (3), with respect to 100 Eq of the epoxy compound, the amount of (meth)acrylic acid should be in the range of 90-110 Eq, or preferably in the range of 90-102 Eq. If the amount of (meth)acrylic acid is smaller than 90 Eq, when the obtained product is used as a coating agent, the crosslinking density during photocuring decreases, and this is undesired. On the other hand, if it is larger than 110 Eq, unreacted (meth)acrylic acid is left, leading to poor weatherability.

[0015]

In this reaction, as needed, one may add various additives, such as 2,6-di-t-butyl-4-hydroxytoluene, hydroquinone monomethyl ether, t-butyl catechol, phenothiazine, and other polymerization inhibitors, toluene benzylammonium chloride, triethylamine, benzyldimethylamine, methyltriethylammonium chloride, triphenyl phosphine, tetraethylammonium bromide, and other catalysts, as well as the following solvents with boiling points higher than the reaction temperature added for viscosity adjustment: methylcellosolve acetate, ethyl Cellosolve acetate, butyl Cellosolve acetate, diethylene glycol monoethyl ether acetate, diethylene glycol dimethyl ether acetate, propylene glycol monomethyl ether acetate,  $\gamma$ -butyrolactone, etc.

[0016]

In this case, the amount of the polymerization inhibitor with respect to the reaction feed mixture should be 1 wt% or less, or preferably 0.5 wt% or less. The amount of the catalyst with respect to the reaction feed mixture should be in the range of 0.001-5 wt%, or preferably in the range of 0.001-3 wt%. The amount of the solvent with respect to the reaction feed mixture should be in the range of 5-500 wt%, or preferably in the range of 5-200 wt%. If the amount of the polymerization inhibitor is over 1 wt%, when the product is used as a coating agent, while the crosslinking density rises for the cured coating film, problems such as insufficient hardness,

insufficient adhesion, etc., occur. If the amount of the catalyst is less than 0.001 wt%, gelled substances are generated in the reaction system, and this is undesired. An amount of solvent more than 5 wt% is effective in lowering the viscosity in the reaction. However, if the amount is over 500 wt%, the reaction time will become too long. This is undesired.

[0017]

Conditions for the reaction between said epoxy compound and (meth)acrylic acid are as follows. The reaction temperature should be in the range of 90-130°C, or preferably in the range of 95-125°C, and the reaction time should be in the range of 3-24 h, or preferably in the range of 4-18 h. If the reaction temperature is higher than 130°C and/or the reaction time is longer than 24 h, in order to obtain a feed resin with hue APHA of 300 or lower, it is necessary to use an epoxy resin represented by formula (2) with hue APHA of 200 or lower. On the other hand, if the reaction temperature is lower than 90°C, the reaction time becomes very long. If the reaction time is shorter than 3 h, it is necessary to raise the reaction temperature, and this is undesired. In addition, in order to suppress polymerization in the double bond portion, usually, dry air is blown into the reaction system while the [reaction] is performed.

[0018]

In order to obtain an epoxy compound represented by formula (2) with hue APHA of 300 or lower, or preferably with hue APHA of 200 or lower, for bis(hydroxyphenyl)fluorene used as manufacturing feed material, the hue APHA has to be 200 or lower. If the hue APHA of bis(hydroxyphenyl)fluorene as manufacturing feed material is over 200, it becomes difficult to obtain the desired epoxy compound with hue APHA of 300 or lower. Also, in order to obtain said bis(hydroxyphenyl)fluorene with hue APHA of 200 or lower, it is necessary to distill and purify the fluorene, a manufacturing feed material, so contents of alkali and heavy metals in the oxidation catalyst will be less than 1 wt%, or to make use of bisphenol prepared by purification and recrystallization as bisphenol, a manufacturing feed material.

/5

[0019]

In addition, in order to obtain the epoxy compound represented by the following formula (2) with hue APHA of 300 or lower, or preferably hue APHA of 200 or lower, it is necessary to suppress the amount of fluorene left in the bis(hydroxyphenyl)fluorene as a manufacturing feed material to less than 1 wt%. In addition, during glycidyl etheriation, one should use nitrogen or other inert gas to replace the interior of the reaction system so as to remove oxygen from the reaction system, and one should perform the operation for removing the residual epichlorohydrin



after glycidyl etherization at 150°C or lower temperature, and perform removal of solvent in the last step at 180°C or lower temperature.

[0020]

By adding at least a polymerization initiator to the acrylate resin for optical material made of fluorene hydroxypropyl acrylate resin with hue APHA of 300 or lower, one can obtain a coating material for protecting transparent plastics, a material for color filters, or an adhesive for optical material, to be explained below.

[0021]

First of all, in order to prepare a coating material for protecting transparent plastics, one should add a polymerization initiator as a necessary component to said acrylate resin for optical material of this invention. In addition, as needed, one may add crosslinking agents for improving hardness and adhesion property, reactive diluting agent, leveling agent, etc., for adjusting viscosity, etc.

[0022]

Types of polymerization initiators for preparing coating material for protecting transparent plastics include photopolymerization initiators and thermal polymerization initiators. Specific examples of photopolymerization initiators include benzophenone, 2,2-dimethoxy-2-phenyl acetophenone, 2,2-diethoxy-2-phenyl acetophenone, 2-ethyl anthraquinone, 2,4-diethylthioxanthone, diisopropyl thioxanthone, benzyl dimethyl ketal, 2-hydroxycyclohexylphenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one, etc.

[0023]

Types of thermal polymerization initiators include the conventional peroxide-based initiators and azobis based initiators. Specific examples of the -based initiators include methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, cyclohexanone peroxide, methylcyclohexane ketone peroxide, acetylacetone peroxide, and other ketone peroxides, isobutyl peroxide, m-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide,  $\alpha$ -methylbenzoyl peroxide, bis-3,5,5-trimethylhexanoyl peroxide, and other diacyl peroxides, 2,4,4-trimethylpentyl-2-hydroperoxide, diisopropyl benzene hydroperoxide, cumene hydroperoxide, t-butyl hydroperoxide, and other hydroperoxides, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 1,3-bis(t-butylperoxyisopropyl)benzene, t-butylcumyl peroxide, and other dialyl peroxides, 1,1-di-t-butylperoxy-3,3,5-trimethylcyclohexane,

2,2-di-(t-butylperoxy)butane, 4,4-di-t-butylperoxyvaleric acid n-butyl ester, and other peroxy ketals, 2,4,4-trimethylbenzylperoxyphenoxyacetate,  $\alpha$ -cumylperoxyneodecanoate, t-butylperoxybenzoate, di-t-butylperoxymethyladipate, and other alkyl peresters, di-t-methoxy butylperoxydicarbonate, di-2-ethylhexylperoxydicarbonate, bis(4-t-butylcyclohexyl)peroxycarbonate, diisopropylperoxydicarbonate, and other percarbonates, as well as acetylcyclohexylsulfonylperoxydicarbonate, t-butylperoxyallyl carbonate, etc. Specific examples of azobis-based initiators include 1,1'-azobiscyclohexane-1-carbonitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis(methylisobutyrate),  $\alpha,\alpha'$ -azobis(isobutyronitrile), 4,4'-azobis(4-cyanovaleric acid, etc.

[0024]

These photopolymerization initiators and thermal polymerization initiators may be used either alone or as a mixture of several. As far as their amounts used with respect to 100 parts by weight of the total amount of the acrylate resin for optical material represented by formula (1), the polymeric polyfunctional acrylate compound and the reactive solvent to be explained later are concerned, the former, that is, the photopolymerization initiator, should be in the range of 0.1-30 parts by weight, or preferably 20 parts by weight or less, and the later, that is, the thermal polymerization initiator, should be in the range of 0.1-10 parts by weight. If the amount is less than the aforementioned range, the polymerization rate will fall, and curing may become insufficient. On the other hand, if the amount is over the aforementioned range, the molecular weight of the cured product will decrease, thus the heat resistance will become insufficient, and adhesion to the substrate will become poor.

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[0025]

Examples of crosslinking agents that may be added as needed include the following trifunctional crosslinking agents: tris(acroxy [transliteration] ethyl)isocyanate (M315, product of Toa Gosei K.K.), dipentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, tripentaerythritol tri(meth)acrylate, tripentaerythritol tetra(meth)acrylate, tripentaerythritol penta(meth)acrylate, tripentaerythritol hexa(meth)acrylate, etc. They may be used either alone or as a mixture of several. The proportion of the crosslinking agent depends on the desired application, hardness, other properties, etc. Usually, among the polymeric resin components (excluding contents [sic], filler, solvent, and polymerization initiator) in the resin composition, the proportion should be in the range of 20-90 wt%.

[0026]

Examples of the reactive diluting agents that may be added as needed include ethylene glycol dimethacrylate (EGDM), isobornyl acrylate (IB-XA, product of Kyoei Kagaku K.K.), N-vinylpyrrolione, tetrahydrofurfuryl acrylate (THF-A, product of Kyoei Kagaku K.K.), caprolactone-modified tetrahydrofurfuryl acrylate, etc. They may be used either alone or as a mixture of several. The proportion of the reactive diluting agent added depends on the appropriate viscosity needed for the coating method. Usually, its proportion should be less than 80 wt%.

[0027]

Examples of applications of the transparent plastics protected with the coating material include lenses, LED, plastic films, substrates, optical disks, and other transparent plastic optical materials. For example, it may be coated on the surface using the spin coating method, followed by curing under irradiation with UV light emitted from a high-pressure mercury lamp, xenon lamp, or the like, or curing by heating using a hot plate, oven, IR heating oven, or the like, to form a coating film on the surface of the optical material or the like.

[0028]

For the material to be used as a color filter, the same polymerization initiator as that added to the acrylate resin for optical material of this invention is also added here as a necessary component. In addition, as needed, it is possible to add the following additives: anthraquinone-based pigments, perylene-based pigments, disazo-based pigments, isoindoline-based pigments, halogenated phthalocyanine-based pigments, carbon, titanium carbon, iron oxide, and other pigments, phenol-novolak epoxy resin, cresol-novolak epoxy resin, trisphenolmethane-based epoxy resin, bisphenol A epoxy resin, bisphenol F epoxy resin, and other epoxy resins, as well as epoxy (meth)acrylates obtained in reaction between said epoxy resin and (meth)acrylic acid, product of reaction between said epoxy (meth)acrylate and said polybasic carboxylic acid or its anhydrides, and other resins containing polymeric unsaturated groups, 2-hydroxyethyl (meth)acrylate, benzyl acrylate, dipentaerythritol hexacrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, diethylene glycol (meth)acrylate, and other polymerizable monofunctional and polyfunctional (meth)acrylic esters, said 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, and other photopolymerization initiators, isobutyl peroxide, and other peroxides, N,N-dimethylaminobenzoic acid ethyl ester, N,N-dimethylaminobenzoic acid isoamyl ester, triethanolamine, triethylamine, and other photosensitizers, as well as silane coupling agents, photostabilizers, oxidation inhibitors, and other conventional additives for color filters.

[0029]

The material for color filters of this invention can be used directly without adding a pigment as a resin composition for protective film of color filters. Also, after adding a pigment, it may be used as an ink for color filters. The resin composition for protective film and ink for color filters may be used in the same way as the conventional resin composition for protective film and ink. They can form protective films and fine patterns with high heat resistance and excellent flatness.

[0030]

In addition, for obtaining an adhesive for optical material, the acrylate resin for optical material of this invention is doped with the same polymerization initiator as above as a necessary component, as well as other additives added as needed, such as a reactive diluting agent that provides good adhesion property and tenacity, silane coupling agent for good adhesion with a glass substrate, solvent for adjusting viscosity, sensitizing agent, etc.

[0031]

Examples of the reactive diluting agents added as needed in the adhesive for optical material include 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), tetrahydrofurfuryl (meth)acrylate, isobornyl (meth)acrylate, N-vinylpyrrolidone, etc., for realizing good adhesion property and for adjusting viscosity, triethylene glycol diacrylate (3EGA), urethane acrylate, ester acrylate, epoxy acrylate, etc., for improving tenacity, etc. They may be used either alone or as a mixture of several. The proportion of the reactive diluting agents should be in the range of 5-95 wt%, or preferably in the range of 10-80 wt%.

[0032]

Examples of the silane coupling agents for improving adhesion with glass substrate include  $\gamma$ -(meth)acryloyloxypropyltrimethoxysilane ( $\gamma$ -aSi),  $\gamma$ -glycyloxypropyltrimethoxysilane ( $\gamma$ -Ep),  $\gamma$ -mercaptopropyltriethoxysilane,  $\gamma$ -aminopropyltriethoxysilane, etc. They may be used either alone or as a mixture of several. The proportion of these silane coupling agents with respect to the total amount of the polymeric resin component should be in the range of 0.1-10 wt%, or preferably in the range of 0.1-5 wt%.

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[0033]

Examples of solvents that may be added as viscosity adjusting agent as needed include ethyl Cellosolve acetate (ECA), propylene glycol monomethyl ether acetate (PGMEA), butyl acetate, and other ester-based solvents, cyclohexane, diisobutyl ketone, and other ketone-based

solvents, diethylene glycol dimethyl ether, and other ether-based solvents, toluene, xylene, and other aromatic hydrocarbon-based solvents, isopropanol, and other alcohol-based solvents, etc. They may be used either alone or as a mixture of several. The proportion of the solvents added with respect to 100 parts by weight of the polymer resin component should be in the range of 10-400 parts by weight, or preferably in the range of 10-200 parts by weight. It is preferred that said solvents be removed from the coating film by means of drying or the like after coating and before laminating.

[0034]

For the aforementioned coating material for transparent plastics, material for color filter, and adhesive for optical material, when they are actually used as optical materials, in order to improve the weatherability and heat resistance, one may add one or several additives selected from UV absorbent, optical stabilizer, oxidation inhibitor, thermal polymerization inhibitor, etc.

[0035]

There is no special limitation on the type of UV absorbent used for this purpose. Any UV absorbent that can be homogeneously dispersed in the acrylate resin composition for optical material and can effectively improve weatherability and prevent cracks from occurring may be used, such as benzophenone-based compounds, benzotriazole-based compounds, phenyl salicylate-based compounds, phenyl benzoate-based compounds, cyanoacrylate-based compounds, etc. In particular, compounds with a maximum absorption wavelength in the range of 240-380 nm are preferred for use.

[0036]

Examples of UV absorbents include 2-hydroxybenzophenone, 5-chloro-2-hydroxybenzophenone, 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-n-octoxybenzophenone, 4-dodecyloxy-2-hydroxybenzophenone, 2-hydroxy-4-octadecyloxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, phenyl salicylate, p-tert-butylphenyl salicylate, p-81,1,3,3-tetramethylbutylphenyl salicylate [sic; p-(1,1,3,3-tetramethylbutyl)phenyl salicylate], 3-hydroxyphenylbenzoate, phenylene-1,3-dibenzoate, 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-(2-hydroxy-5-tert-butylphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-3,5-di-tert-butylphenyl)benzotriazole, 2-(2-hydroxy-5-tert-butylphenyl)benzotriazole, 2-(2-hydroxy-4-octyloxyphenyl)benzotriazole, etc. They may be used either alone or as a mixture of several. The proportion of the UV

absorbent depends on the application of the resin composition, film thickness, film on the substrate, etc., and is usually in the range of 1-20 wt%, or preferably in the range of 2-15 wt%.

[0037]

A typical type of optical stabilizer is the hindered amine-based optical stabilizer for polymer use, in particular, those with cyclic hindered amine structure. Examples include 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, 4-hexanoyloxy-2,2,6,6-tetramethylpiperidine, 4-octanoyloxy-2,2,6,6-tetramethylpiperidine, 4-stearoyloxy-2,2,6,6-tetramethylpiperidine, succinic acid-bis(2,2,6,6-tetramethyl-4-piperidyl), sebacic acid-bis(2,2,6,6-tetramethyl-4-piperidyl), phthalic acid-bis(2,2,6,6-tetramethyl-4-piperidyl), trimesic acid-tris(2,2,6,6-tetramethyl-4-piperidyl), etc. They may be used either alone or as a mixture of several. The proportion of optical stabilizer depends on the application of the resin composition, film thickness, film of the substrate, etc., and is usually in the range of 1-20 wt%, or preferably in the range of 2-10 wt%.

[0038]

In addition, the oxidation inhibitors and thermal polymerization inhibitors that are added to inhibit discoloration and thermal polymerization in heating include the conventional types, such as hindered phenol-based compounds, thioether-based compounds, organic phosphorus-based compounds, etc. Examples include Irganox 1010 manufactured by Adeca [transliteration] Argus Co., triphenyl phosphite, etc. The proportion of said oxidation inhibitor and thermal polymerization inhibitor depends on the application, the thermal history in the manufacturing process, etc., and is usually in the range of 0.01-10 wt%, or preferably in the range of 0.01-2 wt%.

[0039]

Embodiment of the invention

In the presence of a basic catalyst, reaction is performed between 9,9-bis(4-hydroxyphenyl)fluorene and epichlorohydrin to form diglycidyl ether (epoxy compound). The epoxy compound is made to react with (meth)acrylic acid to form an acrylate resin for optical material made of acrylate resin with hue APHA of 300 or lower.

[0040]

Polymerization initiator and, as needed, additives for improving weatherability and heat resistance and other additives are added to acrylate resin to prepare a coating material for protecting transparent plastics. Also, polymerization initiator, and, as needed, additives for

improving weatherability and heat resistance, pigment, and other additives are added to said acrylate resin to prepare a material for color filter. In addition, polymerization initiator, and, as needed, additives for improving weatherability and heat resistance and other additives are added to said acrylate resin to prepare an adhesive for optical material.

[0041]

#### Application examples

In the following, this invention will be explained in detail with reference to application examples and comparative examples. In the following application examples and comparative examples, measurement of the hue APHA of the acrylate resin composition was performed for 50 wt% ethyl Cellosolve acetate solution of the target substance of measurement according to JIS K-6901. Also, measurement of the yellowing index (YI) was performed by a chromaticity meter (product of Suga Shikenki K.K.) using a standard C light source. From the 3 stimulus values in the transmitted light, YI was calculated using the equation :  $YI = (1.06X - 1.28Z)/100Y$ .

[0042]

#### Production example 1

75.0 g of the epoxy compound represented by formula (2) with epoxy equivalent of 257 and hue APHA 30, 20.1 g of acrylic acid, 0.029 g of 2,6-di-t-butyl-4-hydroxytoluene, and 0.13 g of triethylbenzylammonium chloride were loaded in a 500-mL flask equipped with a reflux condenser. While dry air was blown in at a rate of 25 mL/min, the contents were heated to 100°C to form a homogeneous sticky solution.

[0043]

Then, while the contents were heated at 116-118°C and were agitated, the epoxy equivalent and acid value were measured at an arbitrary time, and about 0.45 g of acrylic acid was added to make up for the loss due to spraying out from the reaction system. After 14 h, an acrylate resin represented by formula (1) and having hue APHA 50 (hereinafter referred to as “FHPA”) was obtained.

[0044]

#### Application Example 1

A hard coating agent with composition A as a coating material for protecting transparent plastics was prepared by adding the following components into 5 g of FHPA obtained in said Production Example 1: 60 g of dipentaerythritol hexaacrylate (DPHA, product of Nippon Kayaku K.K.) as crosslinking agent, 35 g of ethylene glycol dimethacrylate (EGDM, product of Kyoei

Kagaku K.K.) as reactive diluting agent, as well as 3 g of 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one (Irgacure 907, product of Ciba-Geigy Co.).

[0045]

Said hard coating agent with composition A was coated on a polycarbonate plate using a spin coater to form a 7- $\mu$ m-thick coating film, followed by irradiation with light to form a cured film. Then, steel wool test was performed using #0000 steel wool for repeated rubbing under a load of 250 g/cm<sup>2</sup>. The results indicated were good, with no scratches at all.

[0046]

Then, said hard coating agent with composition A was coated on a polycarbonate plate using a spin coater, followed by irradiation of light to form a 7- $\mu$ m-thick coating film. For the obtained coating film, weatherability test was performed on a high-energy xenon weatherometer SC700-WA manufactured by Suga Shikenki K.K. Yellowing index and crack generation time were measured before and after the weatherability test. The results indicated that before the weatherability test, the yellowing index (YI) was 0.31. Then, after 600 h of the weatherability test, the yellowing index (YI) became 0.8, and crack generation time was 750 h.

[0047]

Using epoxy compounds having epoxy equivalent and hue APHA listed in Table 1 and prepared in Production examples 2 and 3 and Comparative Production Examples 1 and 2, FHPA samples of the production examples and Co-FHPA samples of the comparative production examples having hue APHA listed in Table 1 were prepared in the same operation as in Production example 1.



[0048]

Table 1

	原料エポキシ化合物の性状 <sup>①</sup>		生成物の略号と色相 <sup>②</sup>	
	色相(APHA) <sup>③</sup>	エポキシ当量 <sup>④</sup>	略号 <sup>⑤</sup>	色相(APHA) <sup>③</sup>
⑥ 製造例 1	30	257	FHPA1	50
" 2	80	254	FHPA2	100
" 3	120	258	FHPA3	270
⑦ 比較製造例 1	400	261	Co-FHPA1	400
" 2	500	247	Co-FHPA2	400

⑧ (注) FHPA: フルオレンヒドロキシプロピルアクリレート樹脂

- Key: 1 Properties of feed epoxy compound  
 2 Abbreviation and hue of product  
 3 Hue  
 4 Epoxy equivalent  
 5 Abbreviation  
 6 Production Example  
 7 Comparative Production Example  
 8 (Note) FHPA: Fluorene hydroxypropyl acrylate resin

[0049]

#### Application Examples 2-9 and Comparative Examples 1-6

Using FHPA and Co-FHPA manufactured in Production examples 1-3 and Comparative production examples 1 and 2, hard coating agents with compositions A-C listed in Table 2 were prepared as coating materials for protecting transparent plastics by adding the following additives: dipentaerythritol hexaacrylate (DPHA, product of Nippon Kayaku K.K.) as hexafunctional crosslinking agent, tris(acroxyethyl)isocyanurate (M315, product of Toa Gosei K.K.) as tri-functional crosslinking agent, ethylene glycol dimethacrylate (EGDM, product of Kyoei Kagaku K.K.) as reactive diluting agent, isobornyl acrylate (IB-XA) also as a reactive diluting agent, and Irgacure 907 as a photopolymerization initiator. For all of said hard coating agents with compositions A-C, several or tens of scratches were observed in the steel wool test.

[0050]

Table 2

	① ハードコート剤の組成 (g : 重量部)					
	FHPA	DPHA	EGDM	M315	IB-XA	Irg907
A	5	60	35	—	—	3
B	5	40	—	40	15	3
C	30	50	20	—	—	3

②(注) FHPA: フルオレンヒドロキシプロピルアクリレート樹脂  
 DPHA: ジペンタエリスリトールヘキサアクリレート (日本化薬社製)  
 EGDM: エチレングリコールジメタクリレート (共栄社化学社製)  
 M315: トリス(アクロキシエチル)イソシアネレート (東亜合成社製)  
 IB-XA: イソボルニルアクリレート (共栄社化学社製)  
 Irg907: イルガキュア-907 (チバガイキ社製)

Key: 1 Composition of hard coating agent (g: parts by weight)

2 (Notes)

FHPA: fluorene hydroxypropyl acrylate resin

DPHA: dipentaerythritol hexacrylate (product of Nippon Kayaku K.K.)

EGDM: ethylene glycol dimethacrylate (product of Kyoei Kagaku K.K.)

M315: tris(acroxyethyl)isocyanurate (product of Toa Gosei K.K.)

IB-XA: isobornyl acrylate (product of Kyoei Kagaku K.K.)

Irg907: Irgacure-907 (product of Ciba-Geigy Co.)

[0051]

For the hard coating agents prepared in Application Examples 2-9 and Comparative Examples 1-6 with compositions A-C, weatherability test was performed in the same way as in said Application Example 1. The yellowing index and crack generation time were measured before and after the weatherability test. The results are listed in Table 3, together with the results for said Application Example 1.

[0052]

	① FHPA略号	② ハ-ド -ト剤 の組 成	③ 耐候性試験結果				
			試験前 YI値④	400h 後YI値⑤	600h 後YI値⑥	クラック発生 時間(hr)⑦	
⑧ 実 施 例	1	FHPA1	A	0.31		0.8	750
	2	"	B	0.4		0.9	1500
	3	"	C	0.9	1.5		650
	4	FHPA2	A	0.5		1.2	750
	5	"	B	0.58		1.4	1200
	6	"	C	1.2	1.7		600
	7	FHPA3	A	0.7		1.5	750
	8	"	B	0.7		1.7	1200
	9	"	C	1.5	2		600
⑨ 比 較 例	1	Co-FHPA1	A	1		3.6	600
	2	"	B	1.1		4	900
	3	"	C	1.8	7		400
	4	Co-FHPA2	A	1.3		1**	450
	5	"	B	1.4		6	800
	6	"	C	2	9		400

⑩(注) YI値: 黄変度の値  
 #1): クラック発生を測定せず。

- Key: 1 Abbreviation of FHPA  
 2 Composition of hard coating agent  
 3 Results of weatherability test  
 4 YI value before test  
 5 YI value after 400 h  
 6 YI value after 600 h  
 7 Crack generation time (h)  
 8 Application Example  
 9 Comparative Example  
 10 (Notes)  
 YI value: Yellowing index value  
 #1) Measurement was not performed due to generation of cracks.

[0053]

#### Application Examples 10-17 and Comparative Examples 7-10

Using FHPA1 and 3 and Co-FHPA1 manufactured in Production Examples 1 and 3 and Comparative Production Example 1, adhesives with compositions D-G listed in Table 4 were prepared as adhesives for optical material by adding the following additives: 2-hydroxyethyl acrylate (HEMA) as a reactive diluting agent, triethylene glycol diacrylate (3EGA) also as a reactive diluting agent, tris(acroxyethyl)isocyanurate (M315, product of Toa Gosei K.K.),

$\gamma$ -acryloyloxypropyltrimethoxysilane ( $\gamma$ -aSi), and Irgacure 907 as a photopolymerization initiator.

[0054]

/10

Table 4

	① 接着剤の組成 (g : 重量部)					
	FHPA	HEMA	3EGA	M315	$\gamma$ -aSi	Irg907
D	66	33	—	—	9	3
E	50	50	—	—	7	3
F	25	—	75	—	3	3
G	30	40	—	30	7	3

② (注) FHPA: フルオレンヒドロキシプロピルアクリレート樹脂  
 HEMA: 2-ヒドロキシエチルアクリレート  
 3EGA: トリエチレングリコールジアクリレート  
 M315: トリス(アクリロキシエチル)イソシアネレート (東亜合成社製)  
 $\gamma$ -aSi:  $\gamma$ -7クロロイロキシプロピルトリメトキシシラン  
 Irg907: イルガキュア-907 (チバガイギー社製)

Key: 1 Composition of adhesive (g: parts by weight)

2 (Notes)

FHPA: fluorene hydroxypropyl acrylate resin

HEMA: 2-hydroxyethyl acrylate

3EGA: triethylene glycol diacrylate

M315: tris(acryloxyethyl)isocyanurate (product of Toa Gosei K.K.)

$\gamma$ -aSi:  $\gamma$ -acryloyloxypropyl trimethoxysilane

Irg907: Irgacure-907 (product of Ciba-Geigy Co.)

[0055]

For each of the adhesives with compositions D-G prepared in Application Examples 10-17 and Comparative Examples 7-10, the following test was performed. The adhesive was coated and sandwiched between two 5-mm-thick glass plates, with an adhesion area of 12.5 mm x 25 mm and a thickness of 40  $\mu$ m. Then, 500 mj of light emitted from a high-pressure mercury lamp (400 W) were radiated, followed by heat treatment at 100°C for 2 h for bonding. Then, using a high-energy xenon sunshine weatherometer (product of Suga Shikenki K.K.), weatherability test was performed at a black panel temperature of 63°C for 200 h consisting of cycles each included 12 min of raining state and 48 min of dry state. The yellowing index in the bonding initial stage and bonding strength (tensile shear strength at 23°C) were measured before the weatherability test and after 200 h of the weatherability test. The results are listed in Table 5.

[0056]

Table 5

		① FHPA略号	② 接着剤の組成	③ 耐候性試験結果			
				試験前 YI値④	200hrs 後YI値⑤	試験前接 着強度⑥	200hrs後 接着強度⑦
⑧ 実 施 例	10	FHPA1	D	0.6	0.6	98	88
	11	"	E	0.41	0.61	93	85
	12	"	F	0.21	0.4	85	78
	13	"	G	0.6	0.9	100	88
	14	FHPA3	D	0.66	1.1	95	87
	15	"	E	0.52	0.84	92	86
	16	"	F	0.28	0.8	87	75
	17	"	G	0.65	1.2	95	85
⑨ 比 較 例	7	Co-FHPA1	D	1.8	8	95	75
	8	"	E	1.2	6.8	87	75
	9	"	F	0.8	4	85	68
	10	"	G	1.3	8.5	92	70

⑩(注) YI値: 黄変度の値  
接着強度: kg/cm<sup>2</sup>

- Key: 1 Abbreviation for FHPA  
 2 Composition of hard coating agent  
 3 Results of weatherability test  
 4 YI value before test  
 5 YI value after 200 h  
 6 Adhesive strength before test  
 7 Adhesive strength after 200 h of test  
 8 Application Example  
 9 Comparative Example  
 10 (Notes): YI value: Yellowing index value  
 Adhesive strength: kg/cm<sup>2</sup>

[0057]

#### Application Examples 18-23 and Comparative Examples 11-14

Using FHPA1~3 and Co-FHPA1 and 2 manufactured in said production examples and comparative production examples, protective film agents with compositions H and I listed in Table 6 were prepared as protective film agents for color filters by adding the following additives: dipentaerythritol hexaacrylate (DPHA, product of Nippon Kayaku K.K.) as hexa-functional crosslinking agent, tris(acroxy[sic, acryloxy]ethyl)isocyanurate (M315, product of Toa Gosei K.K.) as trifunctional crosslinking agent, ethyl Cellosolve acetate (ECA) as a solvent,  $\gamma$ -acryloyloxypropyltrimethoxysilane ( $\gamma$ -aSi) as a silane coupling agent for improving adhesion property with glass, Michler's ketone (MK) as a sensitizing agent, and Irgacure 907 as a

photopolymerization initiator. For these protective film agents, pressure filtering was performed using a 0.2- $\mu\text{m}$  Teflon filter under a pressure of 0.2 kg/cm<sup>2</sup>.

[0058]

/11

Table 6

	① ガラスフィルター用保護膜剤の組成 (g : 重量部)						
	FHPA	DPHA	M315	ECA	$\gamma$ -aSi	MK	Irg907
H	70	30	—	240	3	1	3
I	70	30	10	250	3	1	3

②(注) FHPA: フォルレンヒドロキシプロピルアクリレート樹脂  
 DPHA: ジペンタエリスリトールヘキサアクリレート (日本化薬社製)  
 M315: トリス(アクリロキシエチル)イソシアネレート (東亜合成社製)  
 ECA: エチルセロソルブアセテート  
 $\gamma$ -aSi:  $\gamma$ -アクリロキシプロピルトリメトキシシラン  
 MK: ミチラーケトン  
 Irg907: イルキュア-907 (チバガイコ社製)

Key: 1 Composition of protective film agent for glass filter (g: parts by weight)  
 2 (Notes)  
 FHPA: fluorene hydroxypropyl acrylate resin  
 DPHA: dipentaerythritol hexacrylate (product of Nippon Kayaku K.K.)  
 M315: tris(acroxy[sic, acryloxy]ethyl)isocyanurate (product of Toa Gosei K.K.)  
 ECA: ethyl Cellosolve acetate  
 $\gamma$ -aSi:  $\gamma$ -acryloyloxypropyltrimethoxysilane  
 MK: Michler's ketone  
 Irg907: IRGACURE-907 (product of Ciba-Geigy Co.)

[0059]

For each of the samples of the protective film agents prepared in said application examples and comparative examples, the following test was performed. The agent was coated with a spin coater on a glass substrate coated with SiO<sub>2</sub>, followed by drying at 80°C for 3 min. Then, for the obtained coating film, exposure was performed with 200 mJ of light at 365 nm, followed by heat treatment at 200°C for 1 h. The obtained coating film has a thickness of 2  $\mu\text{m}$ , and is very uniform, and no gel-like substance was observed.

[0060]

For each of the coating films prepared in the application examples and comparative examples, heat resistance test was performed by heat treatment at 250°C for 1 h in a clean oven. The yellowing index was measured before and after the heat resistance test, with results listed in Table 7 for comparison.

[0061]

Table 7

		① FHPA略号	② 保護膜 剤の組 成	③ 耐熱性試験結果	
				試験前YI値	試験後YI値
⑥ 実 施 例	18	FHPA1	H	0.1 ④	0.8 ⑤
	19	"	I	0.1	0.9
	20	FHPA2	H	0.2	1.2
	21	"	I	0.2	1.2
	22	FHPA3	H	0.4	1.9
	23	"	I	0.4	1.5
⑦ 比 較 例	11	Co-FHPA1	H	1.5	4.9
	12	"	I	1.8	4.3
	13	Co-FHPA2	H	1.8	5.2
	14	"	I	1.9	4.2

⑧ (注) YI値: 黄変度の値

- Key: 1 Abbreviation of FHPA  
 2 Composition of protective film agent  
 3 Results of heat resistance test  
 4 YI value before test  
 5 YI value after the test  
 6 Application Example  
 7 Comparative Example  
 8 (Notes): YI value: Yellowing index value

[0062]

## Effect of the invention

For the acrylate resin composition for optical material of this invention, there is little yellowing in weatherability test and heat resistance test. Consequently, the freedom of choice becomes larger with respect to addition of stabilizer and other additives. Also, for the same amount of addition, the degree of yellowing of the cured film is lowered. In addition, crack generation can be reliably prevented. Consequently, this material can be used preferably as optical materials, such as coating material for protecting transparent plastics, material for color filter, adhesive for optical material, etc.